

PATENT SPECIFICATION

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(54) PROCESS FOR PRODUCING RING-OPENING POLYMERISATION PRODUCTS OF CHLORO-NORBORNENE DERIVATIVES

(71) We, SHOWA DENKO KABUSHIKI KAISHA, a Japanese Company of No. 13—9, Shibadaimon 1-chome, Minato-Ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing ring-opening polymerisation products of chloro-norbornene derivatives and, more particularly, it relates to a process for producing a ring-opening polymerisation product of a chloro-norbornene derivative which comprises subjecting the chloro-norbornene derivative to a ring-opening polymerisation using an improved catalyst system.

Various processes have hitherto been proposed for producing ring-opening polymerisation products of chloro-norbornene derivatives. For example, one such process comprises the polymerisation of norbornene derivatives in the presence of a large amount of an alcohol using a compound of a noble metal such as ruthenium as a catalyst as described in *Journal of Polymer Science*, part A, Vol. 3, 895—905 (1965). However, this process is disadvantageous from an economical and industrial standpoint since the catalyst system used in this process does not always show a sufficient catalytic activity and it requires an expensive noble metal.

U.S. Patent No. 3,859,265 discloses that the ring-opening polymerization products of norbornene derivatives can be produced by polymerizing the norbornene derivatives using a catalyst system composed of an organoaluminum compound and a compound of tungsten, molybdenum or tantalum, and that in this process an organic compound such as an alcohol, a peroxide, etc., can be used as a third component, although the patent does not teach the effects brought about by the use of such a third component.

German Patent Application (OLS) Nos. 2,444,681 and 2,447,687 disclose that the activity of a catalyst system composed of an organometallic compound and a compound of tungsten, molybdenum, rhenium or tantalum can be improved by adding to the catalyst system a carbonyl compound or a compound of vanadium, chromium or manganese, or further a compound of a metal of Group IVB or VIII of the Periodic Table.

However, in the case of producing a ring-opening polymerization product by a metathesis polymerisation, i.e., transalkylidenation reaction, of a norbornene compound, the activity of the catalyst system used varies greatly depending upon the presence or absence of a polar substituent or upon the type of polar substituent, if it is present, and thus even if an organic compound (third component) is effective for a certain specific norbornene compound, it is difficult to say that such a third component is always effective for a norbornene compound having other polar groups.

For example, U.S. Patent No. 3,859,365 and German Patent Application (OLS) Nos. 2,444,681 and 2,447,687 set forth above do not specifically disclose examples of the effects of third components in the polymerization of chloro type norbornene compounds, and thus the effect of the addition of the third component in such a polymerization is not apparent from the above patent and patent applications.

In the case of producing polymers, it is generally important to use a catalyst system having high polymerization activity since in such a case the amount of

catalyst used can be reduced as compared with the amount required for a catalyst system having low polymerization activity, which eventually results in reducing the cost of the catalyst employed and in reducing the amount of catalyst residue in the polymer product after polymerization is completed. This is particularly important in practicing polymerization on an industrial scale. For example, if catalyst remains in a polymer product in a large amount, high cost and substantial labour are required to remove the residual catalyst from the polymer product after polymerisation is completed. Further, sufficient removal of residual catalyst becomes more and more difficult with increased amounts of catalyst. In such a case, a considerable proportion of catalyst remains in the polymer product, and such residual catalyst adversely affects the polymer product, for example, giving rise to undesirable colouration of the polymer product as well as enhancing colouration of the product when the polymer product is kneaded while heating or moulded; in general, the polymer product is deteriorated.

According to the present invention, there is provided a process for the ring-opening polymerisation of a chloro-norbornene derivative which comprises subjecting one or more chloro-norbornene derivatives having at least one chlorine atom or a hydrocarbon group substituted with one or more chlorine atoms or a mixture of said chloro-norbornene derivative and at most 50 mole percent of one or more other polymerizable unsaturated cyclic compounds to a ring opening polymerization using a catalyst system prepared from (A) a compound containing a metal-hydrogen and/or metal-carbon bond, said metal being of Group IA, IIA, IIB, IIIB, IVA, or IVB of the Periodic Table (the long form as set out in Encyclopaedia Britannica); (B) a transition metal compound of at least one of tungsten, molybdenum, rhenium tantalum, and niobium, and (C) at least one of water, an epoxide, an acetal, an orthocarboxylic acid ester, a carboxylic acid anhydride, a carboxylic acid ester, a carbonic acid ester, an ether, an aromatic nitrogen-containing heterocyclic compound, an acid amide, a compound having an N—O bond, an amine, or a phosphorus-containing organic compound, the molar ratio of said (A): (B): (C) being 0.2 to 30.0:1:0.02 to 10.0.

In the accompanying drawings:—

Figure 1 shows the infrared absorption spectrum of a polymer obtained by the ring-opening polymerisation described in Example 1, and

Figure 2 shows the NMR spectrum of the polymer obtained by the ring-opening polymerization described in Example 1.

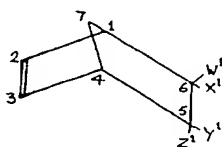
Since the catalyst system used in this invention has a high polymerization activity (catalytic activity) and provides high yields of ring-opening polymerization product per unit amount of catalyst (in other words, the use of a comparatively small amount of the catalyst is sufficient to produce large amounts of ring-opening polymerization product), the amount of the catalyst used can be reduced and production efficiency can be increased.

Further, since the amount of catalyst present in the polymerization system is small, due to the small amount of catalyst employed, the proportion of the residual catalyst in the ring-opening polymerization product after polymerization is also low. Accordingly, removal of residual catalyst to prevent coloring and deterioration of the polymer product is easy.

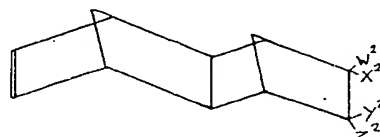
Furthermore, the catalyst system used in this invention shows less reduction in catalytic activity (long catalyst life) during the ring-opening polymerization, which enables the continuous ring-opening polymerization for long periods of time.

The term "hydrocarbon group" as hereafter used refers to a group having the indicated carbon numbers selected from an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group and an aralkyl group.

Typical examples of chloro-norbornene derivatives used as monomers for producing ring-opening polymerization products in the process of this invention are monomers represented by general formulae (I) or (II).



(I)



(II)

wherein W^1 , X^1 , Y^1 , Z^1 , W^2 , X^2 , Y^2 , and Z^2 , which may be the same or different, each represents a hydrogen atom, a chlorine atom, or a hydrocarbon group having at most 20 carbon atoms selected from an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, and an aralkyl group, each of the above hydrocarbon groups may be substituted with one or more chlorine atoms and at least one of W^1 , X^1 , Y^1 and Z^1 or at least one of W^2 , X^2 , Y^2 and Z^2 is a chlorine atom or a hydrocarbon group substituted with one or more chlorine atom(s).

Examples of the hydrocarbon groups represented by W^1 , X^1 , Y^1 , and Z^1 in general formula (I) and W^2 , X^2 , Y^2 , and Z^2 in general formula (II) are methyl, ethyl, n-propyl, isobutyl, n-butyl, hexyl, octyl, dodecyl, tetradecyl, hexadecyl, eicosyl, phenyl, naphthyl, tolyl, cyclohexyl, 2-methylcyclohexyl, and 2-octenyl groups.

Typical examples of the chloro-norbornene derivatives used in this invention as a starting material are 5-chloro-bicyclo[2,2,1]-heptane-2; 5-chloromethyl-bicyclo[2,2,1]-heptane-2; 5-chloro-5-methyl-bicyclo[2,2,1]-heptane-2; 5-chloro-6-methyl-bicyclo[2,2,1]-heptane-2; 5-chloromethyl-6-methyl-bicyclo[2,2,1]-heptene-2; 5- α -chloroethyl-bicyclo[2,2,1]-heptene-2; 5- β -chloroethyl-bicyclo[2,2,1]-heptene-2; 5-chloromethyl-5-methyl-bicyclo[2,2,1]-heptene-2; 5,5-dichloro-bicyclo[2,2,1]-heptene-2; 5,6-dichloro-bicyclo[2,2,1]-heptene-2; 5,5-dichloro-6-methyl-bicyclo[2,2,1]-heptene-2; 5-chloro-6-chloromethyl-bicyclo[2,2,1]-heptene-2; 5,6-dichloro-5-methyl-bicyclo[2,2,1]-heptene-2; 5-(α,β -dichloroethyl)-bicyclo[2,2,1]-heptene-2; 5-chloro-5-methyl-6-chloromethyl-bicyclo[2,2,1]-heptene-2; 5,6-dichloromethyl-bicyclo[2,2,1]-heptene-2; 5,5-dichloromethyl-bicyclo[2,2,1]-heptene-2; 5-chloromethyl-5-methyl-6-chloro-bicyclo[2,2,1]-heptene-2; 5,5,6-trichloro-bicyclo[2,2,1]-heptene-2; and 5,5,6,6-tetrachloro-bicyclo[2,2,1]-heptene-2.

Among these chloro-norbornene derivatives, the use of the norbornene derivatives having two or more chlorine atoms is suitable since they provide ring-opening polymerization products possessing excellent heat resistance and flame retardant capability. A maximum of 10 chlorine atoms per molecule of the chloro type monomer is generally preferred.

In the process of this invention, ring-opening polymerization products can be obtained by subjecting one or more chloro-norbornene derivatives as described above to a ring-opening homopolymerization or a mutual ring-opening copolymerization. The chloro-norbornene derivatives may also be subjected to ring-opening polymerization together with less than 50 mole percent of one or more other unsaturated cyclic compounds.

The unsaturated cyclic compounds which can be copolymerized together with the above chloro-norbornene derivatives in the ring-opening polymerization are cyano-norbornene derivatives, ester-norbornene derivatives, ether-norbornene derivatives, acid anhydride-norbornene derivatives, imide-norbornene derivatives, amide-norbornene derivatives, aromatic norbornene derivatives, aromatic dimethanooctahydronaphthalene derivatives, aromatic norbornadiene derivatives, and ester-norbornadiene derivatives. These unsaturated cyclic compounds may be used alone or as a mixture thereof in the ring-opening polymerization with the aforesaid chloro-norbornene derivatives.

Typical examples of cyano-norbornene derivatives used in this invention as the comonomers for producing ring-opening polymerization products are represented by general formulae (I) and (II) earlier described, wherein W^1 , X^1 , Y^1 , Z^1 , W^2 , X^2 , Y^2 , and Z^2 , which may be the same or different, each represents a hydrogen atom, a cyano group (nitrilo group), or a hydrocarbon group having at most 20 carbon atoms selected from an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, and an aralkyl group, wherein said hydrocarbon group may have or be free of a cyano group, with the proviso that at least one of W^1 , X^1 , Y^1 , and Z^1 in general formula (I) and at least one of W^2 , X^2 , Y^2 , and Z^2 in general formula (II) is a cyano group or a hydrocarbon group substituted with a cyano group.

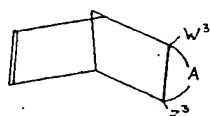
Typical examples of the cyano-norbornene derivatives used as the comonomers for producing ring-opening polymerization products in this invention are 5-cyano-bicyclo[2,2,1]-heptane-2; 5,5-dicyano-bicyclo[2,2,1]-heptane-2; 5,6-dicyano-bicyclo[2,2,1]-heptane-2; 5-cyano-5-methyl-bicyclo[2,2,1]-heptene-2; 5-cyano-6-methyl-bicyclo[2,2,1]-heptene-2; 5-cyano-5-ethyl-bicyclo[2,2,1]-heptene-2; 5-cyano-5-octyl-bicyclo[2,2,1]-heptene-2; 5-cyano-6-phenyl-bicyclo[2,2,1]-heptene-2; 5-cyano-5,6-dimethyl-bicyclo[2,2,1]-heptene-2; 5-cyano-methyl-bicyclo[2,2,1]-heptene-2; 5- ω -cyanoheptyl-bicyclo[2,2,1]-heptene-2; 5-cyano-6-cyclohexyl-bicyclo-

[2,2,1] - heptene - 2; and 5 - ω - cyano - 2 - decenyl - bicyclo[2,2,1] - heptene - 2, with 5 - cyano - bicyclo[2,2,1] - heptene - 2; 5,5 - dicyano - bicyclo[2,2,1] - heptene - 2; 5,6 - dicyano - bicyclo[2,2,1] - heptene - 2; 5 - cyano - 5 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - cyano - 6 - methyl - bicyclo[2,2,1] - heptene - 2; and 5 - cyanomethyl - bicyclo[2,2,1] - heptene - 2 being preferred.

Examples of other cyano-norbornene derivatives which can be used in this invention are described in, for example, U.S. Patent 3,856,758 which corresponds to British Patent Application No. 14697/73 (Serial No.).

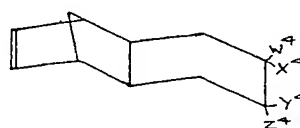
Typical examples of ester-norbornene derivatives used as the comonomers for producing ring-opening polymerization products in this invention are represented by general formulae (I) and (II) shown above, wherein W^1 , X^1 , Y^1 , and Z^1 in general formula (I) and W^2 , X^2 , Y^2 , and Z^2 in general formula (II), each represents a hydrogen atom, an ester group represented by general formula $-\text{COOR}^1$ or $-\text{OCOR}^1$ (where R^1 represents a hydrocarbon group having at most 20 carbon atoms), a hydrocarbon group substituted with an ester group, which is represented by the general formula $-\text{R}^1\text{COOR}^1$ or $-\text{R}^1\text{OCOR}^1$ (where R^1 is as defined above and R^2 represents an alkylene group having at most 20 carbon atoms), or a hydrocarbon group having one and the same meaning as above defined, with the proviso that at least one of said W^1 , X^1 , Y^1 and Z^1 in formula (I) and at least one of said W^2 , X^2 , Y^2 and Z^2 in formula (II) is the ester group or the hydrocarbon group substituted with an ester group as defined above.

Other typical examples of ester-norbornene derivatives used as the monomers for producing ring-opening polymerization products in this invention are represented by general formula (III) and general formula (IV).



(III)

and



(IV)

wherein A represents $-\text{COO}-\text{R}^3-\text{OOC}-$ or $-\text{COOR}^4$ (where R^3 and R^4 each represents an alkylene group having at most 20 carbon atoms); W^3 and Z^3 , being identical or different, each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms, and W^4 , X^4 , Y^4 and Z^4 , which may be the same or different, each represents a hydrogen atom, the ester group as defined above or the hydrocarbon group as described relative to general formula (II), said hydrocarbon group being free of or having the ester group as defined above, at least one of said W^4 , X^4 , Y^4 and Z^4 being the ester group or the hydrocarbon group substituted with the ester group as defined above.

In the practice of the process of this invention, the ester norbornene derivatives represented by general formula (I) are most preferred among the ester-norbornene derivatives shown by above-indicated general formulae (I) or (IV).

Specific examples of the preferred ester-norbornene derivatives of general formula (I) used for producing ring-opening polymerization products in this invention are 5 - methoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - ethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - butoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - allyloxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - methyl - 5 - methoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - hexyloxycarbonyl - 6 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - ethoxycarbonyl - 6 - phenyl - bicyclo[2,2,1] - heptene - 2; 5 - heptyl - 6 - octyloxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - methoxycarbonyl - 6 - methoxycarbonylmethyl - bicyclo[2,2,1] - heptene - 2; 5,6 - dimethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5,6 - diethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5,5 - dibutoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - methyl - 6,6 - dimethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - ω - methoxycarbonylheptyl - 6 - octyl - bicyclo[2,2,1] - heptene - 2; 5 - ω - methoxycarbonyl - 2 - decenyl - 6 - pentyl - bicyclo[2,2,1] - heptene - 2; 5 - ω - methoxycarbonyl - heptyl - 6 - 2 - octenyl - bicyclo[2,2,1] - heptene - 2; 5 - acetoxymethyl - bicyclo[2,2,1] - heptene - 2; 5 - propoxymethyl - bicyclo[2,2,1] - heptene - 2; and 5 - stearoxymethyl - bicyclo[2,2,1] - heptene - 2; with 5 - methoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - ethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - butoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - allyloxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - methyl - 5 - methoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - methoxy-

carbonyl - 6 - methoxycarbonylmethyl - bicyclo[2,2,1] - heptene - 2; 5,6 - dimethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5,6 - diethoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5,5 - dibutoxycarbonyl - bicyclo[2,2,1] - heptene - 2; 5 - acetoxymethyl - bicyclo[2,2,1] - heptene - 2; 5 - propoxymethyl - bicyclo[2,2,1] - heptene - 2; and 5 - stearoxyethyl - bicyclo[2,2,1] - heptene - 2 being preferred.

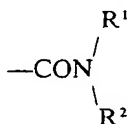
Similarly, specific examples will be easily found about the ester-norbornene derivatives shown by general formulae (II), (III) and (IV) as shown previously.

Typical examples of ether-norbornene derivatives used as the comonomers for producing ring-opening polymerization products in this invention are represented by general formulae (I), (II) and (III) above wherein W^1 , X^1 , Y^1 and Z^1 in general formula (I) and W^2 , X^2 , Y^2 and Z^2 in the above general formula (II), which may be the same or different, each represents a hydrogen atom, an ether group, or a hydrocarbon group substituted with the ether group, which is represented by the general formula $-R^2OR^1$ (where R^1 is as defined above and R^2 represents an alkylene group having at most 20 carbon atoms) or the hydrocarbon group as defined above, with the proviso that at least one of said W^1 , X^1 , Y^1 and Z^1 or at least one of said W^2 , X^2 , Y^2 and Z^2 is an ether group or the hydrocarbon group substituted with an ether group as defined above and W^3 and Z^3 , which may be the same or different, each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms, and A represents $-R^3OR^4-$ or $-R^3O-$ (where R^3 , R^4 and R^5 , which may be the same or different, each represents a divalent hydrocarbon group having at most 20 carbon atoms).

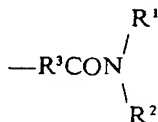
Specific examples of the ether-norbornene derivatives shown by general formula (I) among the ether-norbornene derivatives used as a monomer for producing ring-opening polymerization products in this invention are 5 - methoxy-bicyclo[2,2,1] - heptene - 2; 5 - n - propoxy - bicyclo[2,2,1] - heptene - 2; 5 - isopropoxy - bicyclo[2,2,1] - heptene - 2; 5 - n - butoxy - bicyclo[2,2,1] - heptene - 2; 5 - octoxy - bicyclo[2,2,1] - heptene - 2; 5 - cyclohexoxy - bicyclo[2,2,1] - heptene - 2; 5 - methoxymethyl - bicyclo[2,2,1] - heptene - 2; 5 - isobutoxymethyl - bicyclo[2,2,1] - heptene - 2; 5 - methoxy - 6 - methoxymethyl - bicyclo[2,2,1] - heptene - 2; and 5 - phenoxy - bicyclo[2,2,1] - heptene - 2.

Similarly, practical examples will also be found about the ether-norbornene derivatives represented by general formulae (II) and (III).

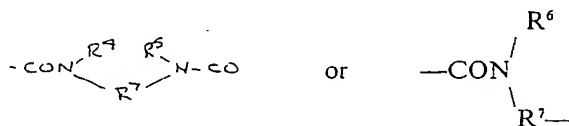
Typical examples of the amide-norbornene derivatives used as the comonomers in this invention are represented by general formulae (I) and (III) indicated above wherein W^1 , X^1 , Y^1 and Z^1 , which may be the same or different, each represents a hydrogen atom, an amide group represented by the general formula



(where R^1 and R^2 , which may be the same or different, each represents a hydrocarbon group having at most 20 carbon atoms, an amide group-containing hydrocarbon residue represented by the general formula

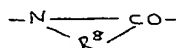


(where R^1 and R^2 have the same meaning as above and R^3 represents an alkylene group having at most 20 carbon atoms), or the hydrocarbon group having the same meaning as above; with the proviso that at least one of said W^1 , X^1 , Y^1 and Z^1 is the amide group or the amide group-containing hydrocarbon residue as above defined; A in general formula (III) represents



(where R^4 , R^5 , and R^6 , which may be the same or different, each represents a hydrocarbon group having at most 20 carbon atoms and R^7 represents an alkylene group having at most 20 carbon atoms); and W^3 and Z^3 in general formula (III), which may be the same or different, each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms.

Furthermore, in the present invention the amide-norbornene derivatives of general formula (I) indicated above wherein at least one of W^1 , X^1 , Y^1 and Z^1 is a group represented by the general formula

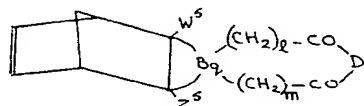


(where R^8 represents an alkylene group having at most 20 carbon atoms) may be used as the comonomer.

Specific examples of the amide-norbornene derivatives used as the monomers for producing ring-opening polymerization products in this invention are N,N - dimethyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N - dibutyl-bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N - methyl - N - octyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N - methyl - N - cyclohexyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N - dicyclohexyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N - dibenzyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N-dimethyl - 5 - methyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N - diethyl-6 - methyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N - dimethyl - 6-phenyl - bicyclo[2,2,1] - heptene - 2 - carbonamide - 5; N,N,N',N' - tetramethyl-bicyclo[2,2,1] - heptene - 2 - dicarbonamide - 5,6; and N,N,N',N' - tetraethyl-bicyclo[2,2,1] - heptene - 2 - dicarbonamide - 5,6.

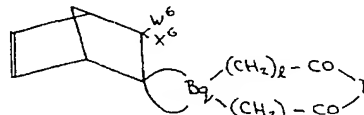
Other examples of the amide type norbornene derivatives which can be used in this invention are described in Japanese Patent Application Publication No. 153100/75.

Typical examples of the acid anhydride norbornene derivatives used as the comonomers in this invention are shown by general formula (V) and (VI).



(V)

and



(VI)

wherein W^5 and Z^5 or W^6 and X^6 , which may be the same or different, each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms; B represents a tetraivalent hydrocarbon group having 4 to 20 carbon atoms; D represents an oxygen atom; l and m each represents independently 1 or 2; and q represents 0 or 1.

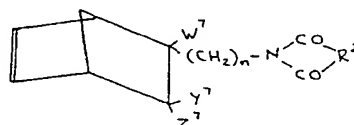
When q is 0 in aforesaid general formulae (V) and (VI), the carbon atoms of the norbornene ring form a single ring together with the acid anhydride-containing group.

Specific examples of the acid anhydride-norbornene derivatives used as the monomers for producing ring-opening polymerization products in this invention are 3,6 - methylene - 1,2,3,6 - tetrahydro - cis - phthalic anhydride; 5 - (5 - carboxy - bicyclo[2,2,1] - hepta - 2 - enyl)acetic anhydride; 2 - oxa - 1,3 - dioxo - 5,8-methano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene; 5,8 - methano-1,2,3,4,4a,5,8,8a - octahydronaphthalene - 2,3 - dicarboxylic anhydride; 1,4,5,8-dimethano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene - 2,3 - dicarboxylic anhydride; 2 - oxa - 1,3 - dioxo - 5,8,9,10 - dimethano - 1,2,3,4,4a,5,8,8a,9,9a,10,10a-dodecahydroanthracene; 3,6 - methano - 1 - methyl - 1,2,3,6 - tetrahydro - cis-phthalic acid anhydride; 3,6 - methano - 1 - butyl - 1,2,3,6 - tetrahydro - cis-phthalic anhydride; and 3,6 - methano - 1 - octyl - 1,2,3,6 - tetrahydro - cis-phthalic anhydride, with 3,6 - methylene - 1,2,3,6 - tetrahydro - cis - phthalic anhydride; 5,8 - methano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene - 2,3 - dicarboxylic anhydride; 1,4,5,8 - dimethano - 1,2,3,4,4a,5,8,8a - octahydro - naphthalene - 2,3 - dicarboxylic anhydride; and 3,6 - methano - 1 - methyl - 1,2,3,6-tetrahydro - cis - phthalic acid anhydride being preferred.

Other examples of acid anhydride-norbornene derivatives which can be used in this invention are described in British Patent Application No. 41299/74 (Serial No. 1,487,185).

Typical examples of the imide-norbornene derivatives used as the comonomers for producing ring-opening polymerization products in this invention are shown by general formulae (V) and (VI) above wherein D represents a group having the general formula >N-R^1 (where R^1 represents a hydrocarbon group having at most 20 carbon atoms or a hydrocarbon group having at most 20 carbon atoms substituted with the above ester group) and B, l, m, and q are as defined above.

Other examples of the imide-norbornene derivatives which can be used in this invention are shown by the following general formula (VII).



(VII)

wherein W^7 , Y^7 and Z^7 , which may be the same or different, each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms; R^2 represents an alkylene group, an alkenylene group or an arylene group, each containing at most 6 carbon atoms; and n represents 0, 1 or 2.

Specific examples of the imide-norbornene derivatives which can be used as the monomers for producing ring-opening polymerization products in this invention are N-methyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-ethyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-propyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-n-butyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-octyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-cyclohexyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-phenyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-methoxycarbonylmethyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-ethoxycarbonyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-butoxycarbonyl-3,6-methylene-1,2,3,6-tetrahydro-cis-1-methyl-1,2,3,6-tetrahydro-cis-phthalimide; N-butyl-3,6-methylene-1-butyl-1,2,3,6-tetrahydro-cis-phthalimide; bicyclo[2,2,1]-hepta-2-ene-5-spiro-3'-N-butylsuccinimide; 2-butyl-2-aza-1,3-dioxo-5,8-methano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; N-octyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene-2,3-dicarboxyimide; 5-maleimidomethyl-bicyclo[2,2,1]-heptene-2,5-citraconimidomethyl-bicyclo[2,2,1]-heptene-2; 5-succinimidomethyl-bicyclo[2,2,1]-heptene-2; and 5-phthalimidomethyl-bicyclo[2,2,1]-heptene-2, with N-methyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-ethyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-propyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-n-butyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-octyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-cyclohexyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; N-phenyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide; and N-octyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene-2,3-dicarboxyimide being preferred.

Furthermore, still other general formulae of imide-norbornene derivatives which can be used as the comonomers in this invention, production processes thereof, typical examples of N-substituted-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide compounds of the imide-norbornene derivatives, the N- ω -(5-norborna-2-enyl)alkyl substituted maleimide compounds thereof, and typical examples of other imide-norbornene derivatives are described in British Patent Application No. 42624/74 (Serial No. 1,448,617).

The norbornene derivatives used as the comonomers for producing ring-opening polymerization products in this invention may contain two or more polar groups which are different from each other, and in such norbornene derivatives, at least two of W^1 , X^1 , Y^1 and Z^1 in general formula (I) or at least two of W^2 , X^2 , Y^2 and Z^2 in general formula (II) can be polar groups selected from cyano groups, ester groups, chlorine atoms, ether groups, imide groups, acid anhydride groups, and amide groups or hydrocarbon substituted with two or more of these polar groups

where at least two polar groups of the norbornene derivative differ from each other. For example, if W¹ among W¹, X¹, Y¹, and Z¹ is a cyano group, one of X¹, Y¹, and Z¹ is a different polar group than the cyano group, such as an ester group, an ether group, and an amide group or a hydrocarbon group substituted with such a different polar group. In this case, further, the norbornene derivative in which X¹, Y¹, and Z¹ are cyano groups only, or hydrocarbon groups substituted with cyano groups only, does not belong to the aforesaid type of norbornene derivative but rather belongs to the cyano-norbornene derivatives.

Also, each of W¹, X¹, Y¹, and Z¹ or W², X², Y², and Z² may be a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms selected from an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group and an aralkyl group.

The object of this invention can be attained by homopolymerization or copolymerization of the above-described norbornene derivatives. Further, these norbornene derivatives can be polymerized with comonomers such as aromatic norbornene derivatives, aromatic nitrogen-containing heterocyclic norbornene derivatives, aromatic norbornadiene derivatives, ester-norbornene derivatives and cycloolefinic compounds.

Typical examples of the aromatic norbornene derivatives which can be used as the comonomers for producing ring-opening polymerization products in this invention are represented by general formula I and II indicated above, wherein W¹, X¹, Y¹, and Z¹ or W², X², Y², and Z², which may be the same or different, each represents a hydrogen atom, an alkyl group having at most 20 carbon atoms, a cycloalkyl group having at most 20 carbon atoms, an alkenyl group having at most 20 carbon atoms or an aromatic hydrocarbon group, which may be substituted with alkyl groups or halogen atoms, having at most 30 carbon atoms, said aromatic hydrocarbon group having at most 3 aromatic rings, and at least one of said W¹, X¹, Y¹, and Z¹ or one of said W², X², Y², and Z² being said aromatic hydrocarbon group. Examples of the formulae of such aromatic hydrocarbon groups are given in Japanese Patent Application Publication Nos. 153100/75 and 160400/75 along with typical examples of the hydrocarbon groups as substituents for the aromatic hydrocarbon groups.

Specific examples of the aromatic-norbornene derivatives which can be used as the monomers for producing ring-opening polymerization products in this invention are 5 - phenyl - bicyclo[2,2,1] - heptene - 2; 5 - methyl - 5 - phenyl-bicyclo[2,2,1] - heptene - 2; 5 - ethyl - 5 - phenyl - bicyclo[2,2,1] - heptene - 2; 5 - n - butyl - 6 - phenyl - bicyclo[2,2,1] - heptene - 2; 5 - p - tolyl - bicyclo[2,2,1] - heptene - 2; 5,6 - diphenyl - bicyclo[2,2,1] - heptene - 2; 5 - α - naphthyl - bicyclo[2,2,1] - heptene - 2; 5 - anthryl - bicyclo[2,2,1] - heptene - 2; 2 - phenyl - 1,4,5,8-dimethano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene; 2 - methyl - 2 - phenyl-1,4, 5,8 - dimethano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene; 2 - p - tolyl-1,4,5,8 - dimethano - 1,3,4,5,4a,5,8,8a - octahydronaphthalene; and 2,3 - diphenyl-1,4, 5,8 - dimethano - 1,2,3,4,4a,5,8,8a - octahydronaphthalene.

Other examples of the aromatic-norbornene derivatives which can be used as the monomers in this invention are described in the above-mentioned Japanese Patent Application Publication.

The aromatic nitrogen-containing heterocyclic norbornene derivatives which can be used as the comonomers for producing ring-opening polymerization products in this invention are norbornene derivatives which contain a heterocyclic ring having at least one nitrogen atom in the ring (see the publication "Aromatic Character" of "Kagaku Dai Jiten (Chemical Encyclopedia)"; Vol. 8, page 601, 1969, published by Kyoritsu Publishing Co.).

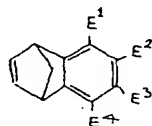
The aromatic nitrogen-containing heterocyclic norbornene derivatives are shown by general formulae I and II indicated above, wherein W¹, X¹, Y¹, and Z¹ in general formula (I) or W², X², Y², and Z² in general formula (II), which may be the same or different, each represents a hydrogen atom; an alkyl group having at most 10 carbon atoms; an aromatic nitrogen-containing heterocyclic group selected from a pyridine group, a quinoline group, and a carbazole group; or such as aromatic nitrogen-containing heterocyclic group substituted by an alkyl group having at most 20 carbon atoms, at least one of said W¹, X¹, Y¹, and Z¹ or at least one of said W², X², Y², and Z² being said aromatic nitrogen-containing heterocyclic group or said alkyl-substituted aromatic nitrogen-containing heterocyclic group.

Specific examples of the aromatic nitrogen-containing heterocyclic norbornene derivatives which can be used as the comonomers in this invention are 5 - (2 - pyridyl) - bicyclo[2,2,1] - heptane - 2; 5 - (3' - pyridyl) - bicyclo[2,2,1]-heptene - 2; 5 - (4' - pyridyl) - bicyclo[2,2,1] - heptane - 2; 5 - (3' - methyl - 2'-

pyridyl) - bicyclo[2,2,1] - heptene - 2; 5 - (4' - methyl - 2' - pyridyl) - bicyclo[2,2,1] - heptene - 2; 5' - (5' - pyridyl) - bicyclo[2,2,1] - heptene - 2; 5 - (2' - ethyl - 3' - pyridyl) - bicyclo - [2,2,1] - heptene - 2; 5 - (3' - butyl - 4' - pyridyl) - bicyclo[2,2,1] - heptene - 2; 5 - (2' - quinoyl) - bicyclo[2,2,1] - heptene - 2; 5 - (3' - quinoyl) - bicyclo - [2,2,1] - heptene - 2; 5 - (4' - quinoyl) - bicyclo[2,2,1] - heptene - 2; 5 - (9' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (3' - methyl - 9 - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (3' - ethyl - 9' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (3' - n - decyl - 9' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (9' - methyl - 3' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (9' - n - butyl - 3' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; 5 - (9' - n - octyl - 3' - carbazolyl) - bicyclo[2,2,1] - heptene - 2; and 2 - (2' - pyridyl) - 1,4, 5,8 - dimethano-1,2,3,4,4a,5,8,8a - octahydronaphthalene.

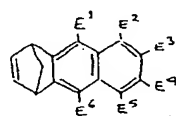
Other examples of typical aromatic nitrogen-containing heterocyclic norbornene derivatives which can be used as the comonomers in this invention are described in Japanese Patent Application Publication No. 110,000/75.

The aromatic norbornadiene derivatives which can be used as the comonomers for producing ring-opening polymerization products in this invention are the norbornene derivatives in which the carbon atoms at the 5- and 6-positions of bicyclo[2,2,1]-heptene-2, i.e., norbornene, concurrently constitute the two adjacent carbon atoms of an aromatic cyclic compound. The aromatic norbornadiene derivatives can be represented by the following general formulae VIII and IX.



(VIII)

and



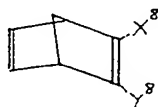
(IX)

wherein E¹, E², E³, E⁴, E⁵, and E⁶, which may be the same or different, each represents a hydrogen atom, a hydrocarbon group selected from an alkyl group having at most 10 carbon atoms, an alkenyl group having at most 10 carbon atoms, a cycloalkyl group having at most 10 carbon atoms, an aryl group having at most 10 carbon atoms, and an aralkyl group having at most 10 carbon atoms, a polar group selected from an ester group having at most 10 carbon atoms and an ether group having at most 10 carbon atoms, or the aforesaid hydrocarbon group substituted with such a polar group.

Specific examples of aromatic norbornadiene derivatives which can be used as the monomers in this invention are 1,4 - dihydro - 1,4 - methanonaphthalene; 1,4 - dihydro - 1,4 - methano - 6 - methylnaphthalene; 1,4 - dihydro - 1,4 - methano - 6 - methoxycarbonylnaphthalene; 5,8 - diacetoxy - 1,4 - dihydro - 1,4 - methanonaphthalene; 5,8 - diacetoxy - 6,7 - dicyano - 1,4 - dihydro - 1,4 - methanonaphthalene; 5,8 - diacetoxy - 6,7 - dimethyl - 1,4 - dihydro - 6,7 - dichloro - 1,4 - dihydro - 1,4 - methanonaphthalene; 1,4 - dihydro - 1,4 - methanoanthracene; and 9,10 - diacetoxy - 1,4 - dihydro - 1,4 - methanoanthracene.

Other typical examples of aromatic-norbornene derivatives which can be used as the comonomers in this invention are described in Japanese Patent Application Publication No. 61,500/75.

Typical examples of ester-norbornadiene derivatives which can be used as the comonomers for producing ring-opening polymerization products in this invention are shown by the following general formula X



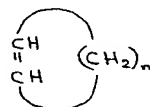
(X)

wherein X⁸ and Y⁸, which may be the same or different, each represents a hydrogen atom; a hydrocarbon group having at most 20 carbon atoms; or the ester-containing group represented by general formula $-(CH_2)_mCOCR'$ or $-(CH_2)_nOCOR''$ (where R' and R'' each represents a hydrocarbon group having at most 20 carbon atoms and m and n each represents 0 or an integer of 1 to 10, at least one of said X⁸ and Y⁸ being such an ester-containing group).

Specific examples of ester-norbornadiene derivatives which can be used as comonomers in this invention are 2-methoxy-carbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-ethoxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-propoxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-butyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-pentyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-hexyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-octyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-decyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-methoxycarbonyl-3-methyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-methoxycarbonyl-3-ethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-dimethoxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-diethoxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-dipropyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-dibutyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-dipentyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-dihexyloxycarbonyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-acetoxymethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-propionyloxymethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-butyryloxymethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-valeryloxymethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-capryloxy-bicyclo[2,2,1]-hepta-2,5-diene; 2-capryloxymethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-di(acetoxymethyl)-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-di(propionyloxymethyl)-bicyclo[2,2,1]-hepta-2,5-diene; 2,3-di(butyryloxymethyl)-bicyclo[2,2,1]-hepta-2,5-diene; 2-methoxycarbonylmethyl-bicyclo[2,2,1]-hepta-2,5-diene; 2-ethoxycarbonylmethyl-bicyclo[2,2,1]-hepta-2,5-diene; and 2-propyloxycarbonylmethyl-bicyclo[2,2,1]-hepta-2,5-diene.

Other unsaturated cyclic compounds which can be used as comonomers for producing ring-opening polymerization products in this invention include monocyclic monoolefinic compounds, non-conjugated cyclic polyene compounds, and polycyclic olefinic compounds.

The monocyclic monoolefinic compounds which can be used as comonomers in this invention are shown by the following general formula (XI)

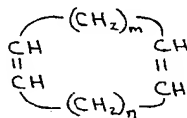


(XI)

wherein n is an integer of 3 or 5 to 20.

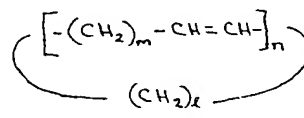
Specific examples of monocyclic monoolefinic compounds which can be used in this invention are cyclopentene, cycloheptene, cyclooctene, cyclodecene, cyclododecene. These monocyclic monoolefinic compounds can each be substituted with at least one hydrocarbon group selected from an alkyl group having at most 10 carbon atoms, an alkenyl group having at most 10 carbon atoms, and an aryl group having at most 10 carbon atoms, at the methylene carbon thereof.

The non-conjugated cyclic polyene compounds which can be used as monomers in this invention are shown by the following general formulae (XII) and (XIII)



(XII)

and



(XIII)

wherein l is an integer of 1—20 and m and n each is an integer of 2—20.

Specific examples of non-conjugated cyclic polyene compounds which can be used as monomers in this invention are 1,5-cyclooctadiene and 1,5,9-cyclododecatriene. Furthermore, the aforesaid non-conjugated cyclic polyene compounds substituted by at least one of the aforesaid hydrocarbon groups and/or a halogen atom may be used in this invention. Typical examples of such compounds are 1-chloro-1,5-cyclooctadiene and 1-methyl-1,5-cyclooctadiene.

Moreover, other examples of the non-conjugated cyclic polyene compounds represented by the aforesaid general formula (XIII) which can be used in the practice of this invention are the oligomers (generally having polymerization degree

of at most 100) obtained by subjecting the cycloolefinic compounds represented by aforesaid general formulae XI or XII to, for example, a metathesis polymerization as described in Journal of Macromolecular Science, Review C—7 (1) P105—109 (1972) MARCEL DEKKER, INC. and U.S. Patent No. 3,074,918.

Still further, polycyclic olefinic compounds which can be used as monomers in this invention can be olefinic compounds having 2 to 10 rings and 1 to 5 carbon-carbon double bonds.

Specific examples of polycyclic olefinic compounds are bicyclo[2,2,1]-heptene -2 (i.e., norbornene); 5 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - vinyl-bicyclo[2,2,1] - heptene - 2; 5 - ethylidene - bicyclo[2,2,1] - heptene - 2; 5 - isopropenyl - bicyclo[2,2,1] - heptene - 2; dicyclopentadiene; bicyclo[2,2,1] - hepta-2,5 - diene (i.e., norbornadiene); and 1,4,5,8 - dimethane - 1,2,3,4,4a,5,8,8a-octahydronaphthalene.

In addition, there are two or more kinds of isomers, the endo type isomer, the exo type isomer and other isomers depending upon the positions of the substituents in the chloro-norbornene derivatives, cyano-norbornene derivatives, the ester-norbornene derivatives, the amide-norbornene derivatives, the acid anhydride-norbornene derivatives, the aromatic-norbornene derivatives, the aromatic nitrogen-containing heterocyclic-norbornene derivatives, the norbornene derivatives having different polar groups, and some of the cycloolefinic compounds (e.g., 5-methyl-bicyclo[2,2,1]-heptene-2) among the above-described monomers used as starting materials in this invention. At the production of ring-opening polymerization products in the process of this invention, these isomers may be separated before use by, for example, rectification or recrystallization, or they may be used without being separated or as a mixture of them.

Among the various unsaturated cyclic compounds described above, preferred compounds are the cyano-norbornene derivatives, ester-norbornene derivatives, ether-norbornene derivatives, amide-norbornene derivatives, aromatic nitrogen-containing heterocyclic norbornene compounds, aromatic norbornene derivatives, and aromatic dimethanooctahydronaphthalene derivatives represented by the general formula I as described with respect to the unsaturated cyclic compounds, wherein the total carbon atom number of W^1 , X^1 , Y^1 and Z^1 summed is at most 8. If the total carbon atom number exceeds 8, the ring-opening polymerization products obtained using such monomers have inferior heat resistance.

Moreover, in the ring-opening polymerization of the imide-norbornene derivative, it is also preferred by the same reason as above to employ the monomer shown by formula V as the main component for the copolymerization. In this case, it is preferred that the carbon atom number of the imide-norbornene derivative be at most 40, in particular, at most 20.

Also, in regard to the acid anhydride norbornene derivatives, it is preferred that the total carbon number thereof be at most 40 as in the aforesaid cases and, in this case, it is more preferred that in the monomers shown by formula V or VI, q is 0 and l and m are 0 or 1, and the total carbon number is 20. In the aromatic-norbornadiene derivatives, it is desirable that the total carbon number be at most 40, in particular less than 20. In particular, in general formula (VII) indicated above, it is preferred that E^1 and E^4 are a hydrogen atom or $—OCOR$ (where, R has at most 5 carbon atoms) and E^2 and E^3 are a hydrogen atom. Furthermore, in the ester-norbornadiene derivatives, it is preferred that the total carbon number be at most 40, particularly less than 30.

When a mixture of a chloro-norbornene derivative and an unsaturated cyclic compound as described above is subjected to a ring-opening polymerization in this invention, the proportion of the unsaturated cyclic compound is at most 50 mole percent based on the total monomers (100 mole percent). If the proportion of the unsaturated cyclic compound is higher than 50 mole percent, the ring-opening polymerization product obtained has inferior flame retardance, and further, the softening point of the product becomes lower when cyclopentene is used as a comonomer in the ring-opening copolymerization.

When an acid anhydride-norbornene derivative is used as the unsaturated cyclic compound or comonomer in the ring-opening polymerization of the chloro-norbornene derivative, it is preferred that the proportion of the derivative be less than 20 mole percent based on the total monomers (100 mole percent). If the proportion of the acid anhydride-norbornene derivative is higher than 20 mole percent, the ring-opening polymerization product obtained has inferior moldability.

Also, when an ester-norbornadiene derivative or an aromatic norbornadiene

derivative is used as the unsaturated cyclic compound, it is preferred that the proportion of the derivative less than 20 mole percent based on the total monomers (100 mole percent). If the proportion of the norbornadiene derivative is higher than 20 mole percent, the ring-opening polymerization product has inferior heat stability.

When an aromatic norbornene derivative is used as the unsaturated cyclic compound, it is preferred that the proportion of the derivative is less than 3 mole percent based on the total monomers (100 mole percent). If the proportion of the aromatic norbornene derivative is higher than 3 mole percent, the ring-opening polymerization product is accompanied by severe gelation, and thus has inferior moldability.

Furthermore, when a monocyclic olefinic compound or a non-conjugated cyclic polyene type compound is used as the unsaturated cyclic compound, it is preferred that the proportion of the compound is less than 20 mole percent based on the total monomers (100 mole percent). If the proportion of the compound is higher than 20 mole percent, the ring-opening polymerization product has lower heat resistance.

Still further, when a polycyclic olefinic compound is used as the unsaturated cyclic compound, it is preferred that the proportion of the compound be less than 30 mole percent based on the total monomers (100 mole percent). If the proportion of the compound is higher than 30 mole percent, the ring-opening polymerization product has inferior moldability.

Of these unsaturated cyclic compounds which can be used as comonomers together with the chloro-norbornene derivatives, cyano-norbornene derivatives, ester-norbornene derivatives, ether-norbornene derivatives, acid anhydride-norbornene derivatives, imide-norbornene derivatives, amide-norbornene derivatives, aromatic-norbornene derivatives and the cycloolefinic compounds are particularly preferred.

As mentioned above, in the present invention, the objects thereof can be attained by subjecting one or more of chloro-norbornene derivatives or a mixture of one or more chloro-norbornene derivative and at most 50 mole percent based on the total monomers (100 mole percent) of the above-mentioned unsaturated cyclic compounds to a ring-opening polymerization using a catalyst system prepared from the organometallic compound, the transition metal compound and the third component as described above.

As described previously, the process of this invention is carried out in the presence of a catalyst system comprising a compound (A), a transition metal compound (B) and a compound (C) as a third component. These compounds are described hereinbelow in greater detail.

Examples of the transition metal compounds used for preparing the catalyst systems in this invention are the compounds composed of at least one of tungsten, molybdenum, rhenium, tantalum and niobium; and hydrogen atoms; halogen atoms; an organic group having at most 10 carbon atoms selected from an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxide group, a phenoxide group, and a carboxylic residue; a cyclopentadienyl group; an acetylacetone residue; carbon monoxide (a carbonyl group); or an acetonitrile group. Further, the complexes of these compounds and pyridine or triphenyl phosphine may be also used as the transition metal compounds. In particular, compounds containing tungsten or molybdenum are preferred, and further compounds containing tungsten are most preferred for the aforesaid purpose.

Specific examples of compounds containing tungsten or molybdenum are tungsten pentachloride, tungsten hexachloride, tungsten pentafluoride, tungsten hexafluoride, tungsten oxytetrachloride, tungsten oxytetrabromide, tungsten oxydichloride, tungsten hexaalcoboholate, tungsten hexaphenolate, tetrachloro-tungsten diphenolate, tetrachlorotungsten dialcoholate, $Al_4W_3Cl_{18}$, molybdenum pentachloride, molybdenum hexachloride, molybdenum pentafluoride, molybdenum hexafluoride, molybdenum pentabromochloride, molybdenum pentabromide, molybdenum oxytrichloride, molybdenum oxytetrachloride, molybdenum dioxydiacetyl acetate, dichloromolybdenum dialcoholate, dichloromolybdenum triphenolate and the like, as described in U.S. Patent 3,856,758 which corresponds to British Patent Application No. 14697/73 (Serial No.).

Further examples of compounds of tungsten or molybdenum are hexacarbonyl tungsten, a complex of tungsten pentachloride and triphenyl phosphine, a complex

of tungsten hexachloride and pyridine, and a complex of tungsten pentacarbonyl and triphenyl phosphine.

5 Examples of transition metal compounds other than compounds of tungsten or molybdenum are rhenium pentachloride, rhenium oxytrichloride, rhenium carbonyl ($\text{Re}(\text{CO})_{10}$), rhenium heptachloride, tantalum pentachloride, tantalum tetrachloride, tantalum trichloride, tantalum oxytrichloride, niobium pentachloride, and niobium pentabromide. 5

10 Further examples of the transition metal compounds used in this invention are the double salts of the aforesaid transition metal compounds and compounds of lithium, sodium, potassium, rubidium, cesium, aluminum, or thallium. Specific examples of such double salts are $\text{LiW}(\text{C}_6\text{H}_5)_6$, $\text{NaW}(\text{C}_6\text{H}_5)_6$, $\text{AlW}(\text{C}_6\text{H}_5)_6$, $\text{Li}_2\text{W}(\text{C}_6\text{H}_5)_6$, $\text{Na}_2\text{W}(\text{C}_6\text{H}_5)_6$, KWCl_6 , RbWCl_6 , CsWCl_6 , and TiWCl_6 . 10

15 The compounds (A) used for preparing the catalyst system in this invention are compounds containing at least one metal belonging to Groups IA, IIA, IIB, IIIB, IVA and IVB of the Periodic Table, and some of these compounds are shown by the formula 15



20 wherein M represents a metal belonging to Group IA, IIA, IIB, IIIB, IVA, or IVB of the Periodic Table; R represents a group having at most 20 carbon atoms selected from an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxide group, a phenoxy group, and a cyclopentadienyl group, or a hydrogen atom, or a halogen atom, wherein the groups represented by R_n may be the same or different and said compound (A) contains at least one metal-hydrogen bond or metal-carbon bond; n represents the maximum atomic valence number of the metal or a positive integer of less than the maximum atomic valence number. 25

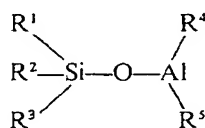
30 Examples of compound (A) which can be used in this invention are complexes of the aforesaid organometallic compounds and an equimolar amount of pyridine, triphenylphosphine, or diethyl ether; the reaction products of 1 mole of the aforesaid organometallic compounds and at most 2.0 moles of water; and complex salts of two kinds of the aforesaid organometallic compounds. 30

35 Typical examples of compound (A) which can be used in this invention are compounds of lithium, sodium, potassium, magnesium, calcium, zinc, boron, aluminium, gallium, titanium, zirconium, silicon, germanium or tin. However, a compound (A) comprising lithium, sodium, magnesium, zinc, aluminium or tin is preferred and, further, organo-aluminium compounds are particularly preferred. 35

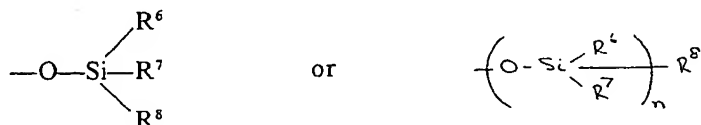
40 Specific examples of preferred organoaluminium compounds are trimethyl aluminium, triethyl aluminium, tri-n-propyl aluminium, tri-isobutyl aluminium, trihexyl aluminium, trioctyl aluminium, tribenzyl aluminium, diethyl aluminium monochloride, di-n-propyl aluminium monochloride, diisobutyl aluminium monochloride, di-n-butyl aluminium monochloride, diethyl aluminium monohydride, diisobutyl aluminium monohydride, di-n-butyl aluminium monohydride, diethyl aluminium monochloride, diisobutyl aluminium monohydride, dibenzyl aluminium monochloride, diethyl aluminium monoethoxide, diisobutyl aluminium monobutoxide, ethyl aluminium sesquichloride, isobutyl aluminium sesquichloride, ethyl aluminium dichloride, isobutyl aluminium dichloride, benzyl aluminium dichloride and ethyl aluminium diethoxide, and a reaction product of triethyl aluminium and water (the molar ratio of water to triethyl aluminium being less than 1.5). Examples of other organoaluminium compounds which can be used in this invention are given in U.S. Patent 3,856,758 (equivalent to British Patent Application No. 14697/73, British Patent Application Nos. 41299/74 and Nos. 41299/74 and 42624/72 (Serial Nos. 1,409,642, 1,487,185 and 1,448,617). 45

50 Still additional examples of organoaluminium compounds are aluminium-siloxalane compounds aluminium-amide compounds, dialumoxane compounds, and double salts containing these organoaluminium compounds. 50

55 The aforesaid aluminium-siloxalane compounds which can be used as the organometallic compounds in this invention are represented by the following general formula 55



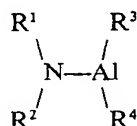
wherein R^1 , R^2 , and R^3 , which may be the same or different, each represents a halogen atom, an alkyl group having at most 10 carbon atoms, or an alkoxy group having at most 10 carbon atoms; R^4 represents an alkyl group having at most 10 carbon atoms; and R^5 represents an alkyl group having at most 10 carbon atoms, an alkoxy group having at most 10 carbon atoms, or a substituent having the formula



(where, R^6 , R^7 , and R^8 , which may be the same or different, each has the same meaning as R^1 , R^2 and R^3 , above, respectively, and n is a positive integer less than 10).

Specific examples of aluminium-siloxalane compounds which can be used in this invention are trimethyldimethyl-siloxalane, trimethyldiethyl-siloxalane, trimethyl-di-n-propyl-siloxalane, trimethyl-diisobutyl-siloxalane, trimethyl-dioctyl-siloxalane, trichlorodimethyl-siloxalane, dimethylethyldiethyl-siloxalane, trimethoxydimethyl-siloxalane, triethyldimethyl-siloxalane, trimethyldimethoxy-siloxalane, trimethyldimethoxy-siloxalane, and trimethoxydichloro-siloxalane.

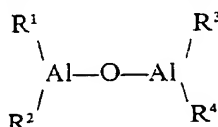
The aluminium-amide compounds which can be used as organometallic compounds in this invention are shown by the following general formula



wherein R^1 , R^2 , and R^3 , which may be the same or different, each represents a hydrogen atom or an alkyl group having at most 10 carbon atoms and R^4 represents a halogen atom or an alkyl group having at most 10 carbon atoms.

Specific examples of the aluminium-amide compounds which can be used in this invention are diethylaluminium dimethylamide, diethylaluminium diethylamide, dimethylaluminium dimethylamide, dimethylaluminium di-n-butylamide, diethylaluminium di-n-butylamide, dichloroaluminium dimethylamide, dimethylaluminium dioctylamide, diisobutylaluminium di-n-butylamide, and dihexylaluminium dioctylamide.

The dialumoxane compounds which can be used as organometallic compounds in this invention are shown by the following general formula



wherein R^1 , R^2 , and R^3 , which may be the same or different, each represents a halogen atom, an alkyl group having at most 10 carbon atoms, or an alkoxy group having at most 10 carbon atoms and R^4 represents an alkyl group having at most 10 carbon atoms.

Specific examples of the dialumoxane compounds which can be used in this invention are tetramethyl dialumoxane, tetraethyl dialumoxane, tetraisobutyl dialumoxane, 1,1-dimethyl-3,3-diethyl dialumoxane, 1,1-dimethyl-3,3-diisobutyl dialumoxane, tetradecyl dialumoxane, trimethyl dialumoxane chloride, and triethyl dialumoxane chloride.

Furthermore, typical and specific examples of compound (A) other than the organoaluminium compounds are n-butyl lithium, phenyllithium, n-amylsodium, cyclopentadienylnsodium, phenylpotassium, diethylmagnesium, ethylmagnesium chloride, methylmagnesium iodide, allylmagnesium chloride, n-propylmagnesium chloride, tert-butyl magnesium chloride, phenylmagnesium chloride, diphenylmagnesium, ethyl ethoxymagnesium, dimethylzinc, diethylzinc, diethoxymagnesium, phenylcalcium iodide, dibutylboron chloride, diborane, trimethylboron, triethylsilane, silicon tetrahydride, triethyl silicone hydride, dimethylgallium chloride,

titanium tetrahydride, titanium tetra-n-butoxide, dicyclopentadienyltitanium dichloride, dicyclopentadienyl zirconium dichloride, tetramethyltin, tetraethyltin, trimethyltin chloride, dimethyltin dichloride, trimethyltin hydride, a complex of ethyl magnesium bromide and ethanol, and the reaction product of diethylzinc and water ($H_2O/Zn(C_2H_5)_2$; 2.0 mole ratio).

Other examples of compound (A) are double salts of two kinds of the aforesaid compounds such as, for example, lithium aluminum tetrahydride and calcium tetraethylzinc.

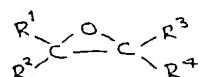
In the practice of this invention, the above-mentioned compounds (A) may be used individually or as a mixture of two or more of such compounds.

As set forth previously the catalyst systems used in the process of this invention contains at least one third component (C) shown below in addition to the above organometallic compound(s) and the transition metal compound(s).

The third component used for the catalyst systems in this invention includes water, epoxide compounds, acetal compounds, orthocarboxylic acid ester compounds, carboxylic acid anhydrides, carboxylic acid ester compounds, carbonic acid ester compounds, ether compounds, aromatic nitrogen-containing compounds, acid amide compounds, compounds having an N—O bond, and phosphorus-containing organic compounds.

Typical examples of the epoxide components used as the third component are ethylene oxide, butene-1-oxide, epichlorohydrin, allylglycidyl ether, and butadiene monooxide.

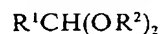
Preferred epoxide compounds include those represented by the formula



wherein R^1 , R^2 , R^3 and R^4 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where an alkyl or alkenyl moiety has at most 10 carbon atoms, and R^1 and R^3 , and/or R^2 and R^4 , when taken together with the carbon atoms to which they are attached, may form a ring.

Typical examples of the acetal compounds are acetaldehyde diethyl acetal, 1,1-diethoxy ethane, dichloroacetaldehyde dimethyl acetal, chloroacetaldehyde diethyl acetal, and acetone dimethyl acetal.

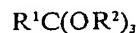
Preferred acetal compounds can be represented by the formula



wherein R^1 and R^2 each represents an alkyl group which may be substituted with one or more halogen atoms, where any alkyl moiety has at most 10 carbon atoms.

Typical examples of the orthocarboxylic acid ester compounds are orthomethyl formate, orthoethyl formate, and orthoethyl acetate.

Preferred orthocarboxylic acid ester compounds can be represented by the formula



wherein R^1 and R^2 each represents an alkyl group which may be substituted with one or more halogen atoms.

Furthermore, typical examples of the carboxylic acid anhydride compounds are the anhydrides of aromatic or aliphatic monohydric carboxylic acids (such as, acetic anhydride, propionic anhydride, butyric anhydride, and benzoic anhydride) and the cyclic acid anhydrides (such as, maleic anhydride, citraconic anhydride, bicyclo[2,2,1]-hept-2-ene-5,6-dicarboxylic anhydride, and hexahydrophthalic anhydride).

Typical examples of the carboxylic acid ester compounds are a carboxylic acid ester of a mono- to trihydric carboxylic acid and a monohydric alcohol or phenol (such as ethyl formate, methyl acetate, methyl caproate, ethyl benzoate, dimethyl succinate, ethyl glutarate, ethyl sebacate, and dimethyl tetraphthalate), and a cyclic ester (such as, γ -butyrolactone and ϵ -caprolactone).

Typical examples of the carboxylic acid ester compounds are carboxylic acid esters of mono- to trihydric hydroxy compounds (such as, esters of alcohols or phenols) and monohydric carboxylic acids.

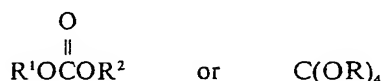
Preferred carboxylic acid ester compound can be represented by the formula



wherein R^1 and R^2 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where any alkyl or alkenyl group has at most 10 carbon atoms, and n is an integer of 1 to 3.

Typical examples of the carbonic acid ester compounds are carbonates of monohydric hydroxy compounds (such as, diethyl carbonate, di-*n*-propyl carbonate, and diphenyl carbonate) and tetraalkyl orthocarbonates (such as, tetramethyl orthocarbonate and tetra-*n*-butyl orthocarbonate).

Preferred carbonic acid ester compound can be represented by the formula



wherein R , R^1 and R^2 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where any alkyl or alkenyl moiety has at most 10 carbon atoms.

Typical examples of the ether compounds are diethyl ether, di-*n*-butyl ether, anisole, and diphenyl ether.

It is preferred that each of the epoxide compounds, the acetal compounds, the orthocarboxylic acid ester compounds, the carboxylic acid anhydrides, the carboxylic acid ester compounds, the carbonic acid ester compounds, and the ether compounds has at most 20 carbon atoms.

Examples of the amine compounds are primary amines such as methylamine, ethylamine, isopropylamine, *n*-butylamine, cyclohexylamine, benzylamine, aniline, and naphthylamine; secondary amines eg dimethylamine, methylethylamine, *N*-methylcyclohexylamine, *N*-methylbenzylamine, *N*-methylaniline, pyrrolidine, diethylamine, dicyclohexylamine, dibenzylamine, and di-*n*-propylamine; tertiary amines eg triethylamine, tri-*n*-butylamine, methyl-di-*n*-butylamine, *N,N*-dimethylcyclohexylamine, *N,N*-dimethylbenzylamine, *N,N*-dimethylaniline, and *N*-ethylpyrrolidine; diamines eg ethylene diamine, trimethylenediamine, hexamethylenediamine, 1,4-cyclohexanediamine, *p*-phenylenediamine, *N,N*-dimethylenediamine, *N,N*-dimethylhexamethylenediamine, piperazine, *N,N,N',N'*-tetramethylethylenediamine, and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; and the *N*-hydrocarbon substituted derivatives thereof.

Examples of nitrogen-containing heterocyclic compounds are pyridine and the alkyl-substituted derivatives thereof eg α -, β -, or γ -picoline, 2,3-lutidine, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, 3,4-lutidine, 2,5-lutidine, 2,3,6-collidine and 2,4,6-collidine and quinoline and the alkyl-substituted derivatives thereof eg 2-methylquinoline, 4-methylquinoline, 6-methylquinoline, 7-methylquinoline, 8-methylquinoline, isoquinoline, and 1-methyl isoquinoline.

The acid amide compounds are carboxylic acid amide compounds of monohydric or polyhydric carboxylic acids and ammonia or a primary or secondary amine eg acetamide, propionamide, hexaneamide, cyclohexane carbonamide, benzamide, *N*-methylacetamide, *N*-methylbenzacetanilide, *N,N*-dimethylformamide, *N*-methylacetanilide, succinamide, adipamide, and maleinamide; cyclic amide compounds eg γ -butyrolactam and ϵ -caprolactam; urea and derivatives thereof eg 1,1-dimethylurea, 1,3-dimethylurea, 1,3-di-*n*-butylthiourea, and tetramethylurea; sulfonamides eg benzensulfonamide and *p*-toluene-sulfonamide; and hexamethylphosphorous triamide.

Examples of compounds having a nitrogen-oxygen bond are *N*-nitroso compounds and *o*-nitroso compounds eg *N*-nitrosodimethylamine, *N*-nitroso-*N*-methylphenylamine, *N*-nitrosodiphenylamine, *n*-amyl nitrite, and isoamyl nitrite and aliphatic nitro compounds and aromatic nitro compounds (nitroaryl) having 1—3 nitro groups and 0—4 chlorine atoms eg nitroethane, 4-chloro-1-nitrotoluene, dinitrophenol, 4-chloro-2-nitroanisole, 1,3-dinitrobenzene, any of amyl nitrate and 1,2-dinitro-3,5-dichlorobenzene. It is preferred that the aforesaid nitrogen-containing organic compounds have at most 20 carbon atoms.

The phosphorus-containing organic compounds used as the third component of the catalyst system have less than 30 carbon atoms and examples thereof are phosphine compounds eg. as tri-*n*-butylphosphine and triphenylphosphine; phosphine

oxide compounds eg. tri-n-butylphosphine oxide and triphenylphosphine oxide; phosphite compounds eg. trimethyl phosphite, triethyl phosphite, and triphenyl phosphite; phosphate compounds eg. trimethyl phosphate, tri-n-butyl phosphate, and triphenyl phosphate; and compounds having a phosphorus-chlorine bond eg. dichlorophenyl phosphine and chlorodiphenyl phosphine.

Of these compounds, epoxide compounds, acetal compounds, orthocarboxylic acid ester compounds, carboxylic acid anhydrides, carboxylic acid ester compounds, carbonic acid ester compounds, ether compounds, aromatic nitrogen-containing compounds, compounds having an N—O bond and phosphorus-containing organic compounds are preferred. The most preferred compounds are epoxide compounds, acetal compounds, orthocarboxylic acid ester compounds, carboxylic acid ester compounds, carbonic acid ester compounds and phosphorus-containing organic compounds.

In the case of preparing the catalyst system used in this invention, the proportion of the aforesaid compound (A) per mole of the transition metal compound is 0.2 to 30.0 moles, preferably 0.5 to 20 moles, most preferably 1.0 to 10.0 moles. If the amount of the compound (A) is less than 0.2 mole per mole of the tungsten or molybdenum compound, a catalyst system possessing sufficient polymerization activity cannot be obtained, while if the amount is more than 30.0 moles, the addition of such an excessive amount of the organometallic compound does not further improve the polymerization activity of the catalyst system and sometimes reduces the activity thereof.

The proportion of the aforesaid third component depends upon the kind of the third component employed, but it is 0.02 to 10.0 moles, preferably 0.05 to 9.0 moles, most preferably 0.1 to 6.0 mole per mole of the transition metal compound.

If the proportion of the third component is less than 0.02 mole per mole of the transition metal compound, the effect of the addition thereof is scarcely obtained, while if the proportion is higher than 10.0 moles, the polymerization activity of the catalyst system sometimes becomes lower.

In the practice of the process of this invention, each catalyst component of the catalyst system may be added as it is to the polymerization system (ring-opening polymerization system) without any pretreatment of the components, but, if desired, one or more of the catalyst components or a mixture thereof may be ground prior to addition to the polymerization system. Further, the catalyst components may be reacted, as described hereinbelow in detail, before use in the polymerization system. Such pretreatment generally increase the catalyst activity of the catalyst system. Furthermore, the pretreated catalyst components or the reaction products of the components may be subjected to, for example, extraction with a solvent such as those used in the catalyst-forming reaction described below and the thus treated products added to the polymerization system.

As described above, the catalyst components can be reacted together before addition to the polymerization system. Reaction is typically in a glass-lined vessel under an inert atmosphere eg. nitrogen gas or argon.

The reaction temperature employed in the above catalyst-forming reaction is generally -100 to 250°C , preferably -40 to 200°C , particularly 10 to 180°C . If the reaction temperature is lower than -100°C , the rate of reaction is low, while if the reaction temperature is higher than 250°C , it does not further contribute to increasing the polymerization activity. The catalyst formation is preferably carried out under autogeneous pressure in a close vessel. Other conditions are given on page 11.

The catalyst-forming reaction may be carried out in an inert organic solvent (the term inert organic solvent meaning an organic solvent which does not cause reaction with the above transition metal compound and the above third component (C) and which is in the liquid state at the reaction temperature). It is preferred that the solvent have a melting point of less than 30°C , more preferably less than 20°C , and more particularly less than 10°C , and have a boiling point of less than 500°C , more preferably less than 400°C , and particularly less than 300°C .

Examples of the inert organic solvents are aliphatic hydrocarbons eg. pentane, hexane, heptane, octane, and decane; alicyclic hydrocarbons eg. cyclopentane and cyclohexane; aromatic hydrocarbons eg. benzene, toluene and xylene; halogenated hydrocarbons eg. methylene chloride, ethyl chloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,2-dichloroethylene, 1-chloropropane, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane, 1-chloropentane, chlorobenzene, o-dichlorobenzene, m-dichlorobenzene and p-chlorobenzene; and ethers eg. diethyl ether and tetrahydrofuran.

In the production of the catalyst system, the ratio of the inert organic solvent to the transition metal compound or the compound (A) employed varies depending upon the reaction conditions, but is generally less than 50 parts by weight, preferably less than 20 parts by weight per one part by weight of the transition metal compound or the compound (A). If more than 50 parts of inert organic solvent is used, it does not contribute to further increase catalytic activity, which makes the use of such a large amount of inert organic solvent profitless.

In the above described reaction for producing the catalyst system, the inert organic solvents described above may be used individually or as a mixture thereof. Furthermore, the transition metal compounds, the compound (A) and the third components each described above may be used individually or as a mixture thereof, respectively.

In the present invention, the above monomer may be subjected to ring-opening polymerization using the catalyst system prepared from the compound (A), transition metal compound and the third component in the absence of an inert organic solvent, if desired (that is, a bulk polymerization), but the ring-opening polymerization may be carried out in an inert organic solvent. It is a matter of course required that the organic solvent used in the polymerization does not injure the catalyst system and does not undergo reaction with the monomer and comonomers used in the invention. It is particularly preferred to use as the solvent the inert organic solvent as used in the reproduction of the catalyst system. Thus, typical examples of the inert organic solvent are those illustrated as the inert organic solvent used for producing the catalyst system. The organic solvents may be used individually or as a mixture thereof.

When the ring-opening polymerization is carried out in the above-described inert organic solvent, the proportion of the organic solvent is generally at most 20 volume parts, preferably less than 10 volume parts, per volume part of the monomer and comonomers. If the proportion of the solvent is higher than 20 volume parts per volume part of the monomers to be polymerized, i.e., norbornene derivatives plus other unsaturated cyclic compounds, it becomes difficult to recover the ring-opening polymerization product obtained after the polymerization is completed. Furthermore, recovery of the organic solvent used is also difficult.

The polymerization temperature is generally from -100°C to 200°C , preferably from -50°C to 150°C , and most preferably from 0°C to 120°C . If the polymerization temperature is lower than -100°C , the rate of polymerization is quite low due to the insufficient polymerization activity in the polymerization system, and thus a long period of time is required to complete the ring-opening polymerization. In this case, further, the mixture of the monomer(s) and the aforesaid inert organic solvent is often solidified. On the other hand, if the polymerization temperature is higher than 200°C , it sometimes is difficult to sufficiently control the polymerization, and further the product tends to be severely colored and its properties are generally not satisfactory.

The amount of the catalyst relative to the monomers (and comonomers) varies depending upon the type of the monomers (and comonomers) as well as the properties of the desired ring-opening polymerization products, but is generally 0.001 to 20 moles, preferably 0.1 to 5 moles, based on the transition metal compound per 100 moles of the monomer (and comonomer).

When catalyst is used in a proportion more than 20 moles based on the transition metal compound, the process is not economical and further no additional improvement is attained in catalytic activity.

In addition, the use of the catalyst system in such a large amount generally makes it difficult to remove the catalyst remaining in the polymerization system upon completion of the ring-opening polymerization, thereby resulting in coloration of the polymers. Such coloration increases when heat is applied in further processing of the polymers which ultimately causes heat-deterioration of the polymers or articles produced from such polymers.

It is preferred to carry out the ring-opening polymerization of this invention under an inert gas atmosphere eg. argon or nitrogen. If oxygen and moisture and present in the polymerization system, the catalyst system is partially or wholly degraded, which makes it impossible to obtain reproducible results.

The ring-opening polymerization of the present invention can be carried out either in an open vessel or in a closed vessel under autogeneous pressure. The time required for completing the polymerization varies depending upon the temperature used, the amount and the type of the catalyst used i.e., whether the catalyst components have previously been reacted each other or not, and the type of the

monomers to be polymerized, but generally a reaction time of 30 minutes to 24 hours provides good results.

By carrying out the ring-opening polymerization in the manner as described above, the desired ring-opening polymerization product(s) can be obtained and, in this case, the molecular weight of the ring-opening polymerization products obtained can be controlled by adding to the polymerization system a molecular weight controlling agent eg. an α -olefin having at most 15 carbon atoms (e.g., ethylene, propylene, butene-1, hexene-1, and octene-1); internal olefins having at most 20 carbon atoms (e.g., butene-2, hexene-2, and octene-2); conjugated diolefins having at most 20 carbon atoms and the halogen-substituted conjugated diolefins (e.g., butadiene, isoprene, and chloroprene); and non-conjugated diolefins having at most 20 carbon atoms (e.g., 1,4-hexadiene). Examples of other molecular weight controlling agents are acetylene compounds having at most 20 carbon atoms eg. 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-butylacetylene, 1-heptyne, 3-octyne, 1-decyne, vinylacetylene, 1,5-hexa-diene, 1,8-non-diene, and 1,9-deca-diene, allene compounds having at most 20 carbon atoms, eg. allene, methylallene, ethylallene, trimethylallene and tetramethylallene, triolefin compound having at most 20 carbon atoms eg. 1,3,5-heptatriene, 1,3,5-octatriene, 1,3,5,7-octatetraene, 3-methyl-1,3,5-heptatriene, 3,4-dimethyl-1,3,5-heptatriene and 1,3,6-octatriene, allyl compound having at most 20 carbon atoms eg. allyl alcohol, allyl ether, allylethyl ether, allylphenyl ether, allylamine, diallylamine, allyl chloride, allyl methacrylate, diallyl oxalate, diallyl malonate and diallyl phthalate, as described in Japanese Patent Application Publications Nos. 56,494/75, 56,495/75, 56,496/75 and 56,497/75.

In the case of using or adding the molecular weight controlling agent, the proportion thereof is generally at most 20 moles, preferably less than 10 moles, most preferably less than 5 moles, per 100 moles of the monomer and comonomers used for the ring-opening polymerization.

The ring-opening polymerization of this invention can be effectively carried out in the absence of an unsaturated polymer, but it can further be carried out in the presence of an unsaturated polymer. The unsaturated polymer used has a carbon-carbon double bond in the polymer and the Mooney viscosity thereof is generally 10 to 200, preferably 20 to 150, more preferably 30 to 130. Also, it is preferred that the unsaturated polymer have at least one carbon-carbon double bond, more preferably more than 10 carbon-carbon double bonds, per 1,000 total carbon-carbon bonds. Examples of such unsaturated polymers are butadiene rubbers containing butadiene as the main component (generally more than 50% by weight), eg. a butadiene homopolymer rubber, a styrene-butadiene copolymer rubber, and an acrylonitrile-butadiene copolymer rubber, chloroprene rubbers, isoprene rubbers, natural rubbers, ethylene-propylene-diene terpolymers (generally called EPT or EPDM). Furthermore, cycloolefinic rubber-like materials prepared by ring-opening polymerizing cycloolefinic compounds may be used for this purpose.

When the ring-opening polymerization of this invention is carried out in the presence of the above unsaturated polymer. Processes of producing such unsaturated polymers and the properties thereof are described in Kanbara et al, "Synthetic Rubber Handbook", 1967, published by Asakura Shoten, and "Encyclopedia Polymer Science and Technology (Plastics, Resins, Rubber, Fibers)" by Harman F. Mark et al, Vol. 1 to 16 (1964—1971) published by John Wiley & Sons, Inc.

The unsaturated polymers used in this invention may be random copolymer rubber-like materials or block copolymer rubber-like materials as in the case of, for example, styrene-butadiene copolymer rubber-like materials.

In the case of carrying out the ring-opening polymerization of this invention in the presence of such an unsaturated polymer, the proportion of the unsaturated polymer is generally at most 1,000 parts by weight, preferably less than 500 parts by weight, more preferably less than 300 parts by weight, per 100 parts by weight of the monomer(s) used. If the proportion of the unsaturated polymer is more than 1,000 parts by weight per 100 parts by weight of the monomer(s), a polymerized product showing the inherent properties possessed by the monomer(s) used is not obtained.

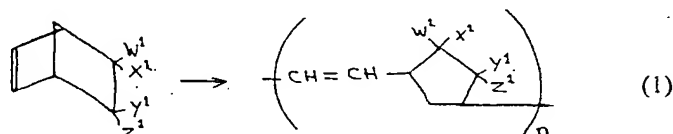
In the practice of the ring-opening polymerization of this invention in the presence of such an unsaturated polymer, the polymer can be used as a solution or suspension (dispersion) thereof in the monomer(s) or a mixture of the monomer(s) and the above described inert organic solvent. Furthermore, the ring-opening

polymerization can be a block polymerization, graft polymerization or a combination of a graft polymerization and a block polymerization.

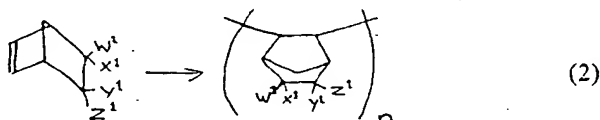
The graft or block polymerization product obtained by practicing the ring-opening polymerization of this invention in the presence of the unsaturated polymer has excellent impact resistance as compared with the ring-opening polymerization product obtained by practicing the ring-opening polymerization of this invention in the absence of the unsaturated polymer, although the extent of the improved impact resistance may differ with the proportion of the unsaturated polymer employed; this embodiment is particularly useful in fields in which high impact resistance is required.

After the ring-opening polymerization is completed, the polymer obtained can be recovered in various manners. In an example of the recovering processes, catalyst removal methods and polymer recovery methods as are conventionally employed in the solution polymerization of isoprene or butadiene. For example, there is a process in which a solution containing the ring-opening polymerization product, the unreacted monomer and the catalyst residue is added to a lower alcohol (e.g., methanol and ethanol) or the alcohol containing a small amount of hydrochloric acid, whereby the catalyst residue is removed and, at the same time, the ring-opening polymerization product obtained is precipitated, and a process in which an organic solvent solution containing the ring-opening polymerization product, the unreacted monomer, and the catalyst residues is uniformly mixed with an inert organic solvent (e.g., methylene chloride) which is immiscible with water, the resulting mixture is treated with water containing a chelating agent (e.g., ethylene-diamine tetraacetic acid and nitrilotriacetic acid) and, after removal of the catalyst residues, the organic solvent is removed from the reaction mixture. Other purification processes (post-treatments) which can be employed for recovering the ring-opening polymerization products of this invention are described in U.S. Patent No. 3,856,758 which corresponds to British Patent Application No. 14697/73 (Serial No. 1,409,642); Japanese Patent Application Publication Nos. 77,999/75 and 130,500/74; British Patent Application No. 41299/74 (Serial No. 1,487,185); British Patent Application No. 42624/74 (Serial No. 1,448,617); Japanese Patent Application Publication Nos. 71800/75, 103,600/75, 153,100/75 and 160,400/75.

The ring-opening polymerization in accordance with the process of this invention using any type of the above catalyst systems generally results in the production of the polymer (1) below by the following scheme wherein a chloro type norbornene derivative, for example, a compound of the formula (1), is subjected to homopolymerization or copolymerization of different monomers.



As is apparent to one skilled in the art, there is a possibility that the chloro type norbornene derivatives defined in the present invention forms a vinylene type polymer (2) below by the following scheme.



wherein W^1 , X^1 , Y^1 and Z^1 are as defined above and n is an integer.

However, in the ring-opening polymerization of this invention, the vinylene type polymer is not substantially produced and, if any, is produced in a very small amount.

The properties of the ring-opening polymerization products purified by the aforesaid process vary according to the kinds of monomer(s), the kinds and the copolymerization ratio of the comonomers in the case of ring-opening copolymerization products, the kind of catalyst, and other polymerization conditions, but the products are usually colorless or light-yellow transparent

polymers. The reduced viscosity of the ring-opening polymerization products (including copolymers) depends upon the polymerization conditions as described above, but is usually 0.1 to 20.0 in dimethylformamide (concentration 0.1 g./dl.) at 30°C. In addition, the product can be obtained as a gel (insoluble in various organic solvents) depending on the polymerization conditions employed.

Since the ring-opening polymerization product obtained in the process of this invention has a reactive double bond in the molecule, another monomer such as styrene, acrylonitrile, methyl methacrylate, etc., can be graft polymerized onto the ring-opening polymerization product. Also, the ring-opening polymerization product thus obtained may be subjected to a crosslinking reaction by heating or by using a crosslinking agent, such as an organic peroxide, to provide a thermosetting resin.

As mentioned above, since the ring-opening polymerization products obtained by the process of this invention are excellent not only in their flame retardant capability but also in their heat resistance and various mechanical properties, they can be used not only individually but as blends thereof with a thermosetting resin having good miscibility therewith, such as a vinyl chloride polymer, a styrene polymer, a methyl methacrylate polymer, an acrylonitrilestyrene copolymer, an acrylonitrile-butadiene-styrene ternary resin (ABS resin), and a graft polymer prepared by grafting acrylonitrile and styrene on to chlorinated polyethylene and/or an elastomer such as a polybutadiene rubber, a styrene-butadiene copolymer rubber (SBR), an acrylonitrile-butadiene copolymer rubber (NBR), a chlorinated polyethylene, a chlorosulfonated polyethylene acryl rubber, and a chloroprene rubber.

Also, if desired, conventional additives as are customarily added to ordinary synthetic resins, such as stabilizers to ultraviolet rays, oxygen, and ozone; flame retardants, plasticizers, lubricants, reinforcing agents; fillers, coloring agents (pigments), coloring improving agents; antistatic agents; and developing promoters can be added.

The ring-opening polymerization product obtained by the process of this invention, the thermosetting resin, the elastomer, and the blend prepared using the product can be fabricated into various shapes by any method generally used for synthetic resins, such as a compression molding method, an extrusion molding method, an injection molding method, a blow molding method, and a casting method.

The ring-opening polymerization products obtained by the process of this invention having various merits as described above can be fabricated or molded into various shapes by various molding methods. For example, they can be used as vessels, films, sheets, packaging materials, parts of articles of daily use and machines and parts of electric instruments. Furthermore, since the ring-opening polymerization products have excellent flame retardant capabilities and heat resistance, they are particularly useful as the parts for televisions, electric calculators, radios, and tape recorders as well as housing.

The invention will now be described in more detail by the following examples.

Example 1

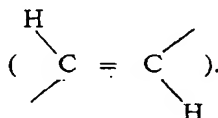
In to a two-liter stainless steel autoclave the atmosphere of which was replaced with nitrogen after drying were placed 191 g. (1.0 mole) of a monomer, 5,6-dichloromethyl-bicyclo[2,2,1]-heptene-2 purified by distillation under reduced pressure by means of a rectification apparatus immediately before use, 0.84 g. (10 millimoles, 1.0 mole % based on monomer) of n-hexene-1, 5.0 ml. (0.2 mole/l.) of a toluene solution of chloroacetaldehyde diethyl acetal as a third component for the catalyst system, and about 600 ml. of a solvent, (1,2-dichloroethane dehydrated using potassium hydrate and purified by distillation immediately before use), followed by stirring to provide a homogeneous solution. After cooling the reaction system on an ice bath, 3.0 ml. of a toluene solution of diethylaluminum chloride (concentration of 1 mole/liter; containing 3.0 millimoles of diethylaluminum chloride) and 2.5 ml of a toluene solution of tungsten hexachloride (concentration 0.2 mole/l.; tungsten hexachloride: 0.5 millimole) were added with stirring to the reaction system as catalyst components 6 moles of diethylaluminum chloride and 6 moles of chloroacetaldehyde diethyl acetal were present per one mole of tungsten hexachloride. Then, after removing the ice bath, the polymerization reaction was carried out for 30 minutes at 60°C with stirring.

After the polymerization was completed, bis(2-hydroxy-3-tertiary-butyl-5-methylphenyl) methane was added to the reaction mixture (a solution containing

the ring-opening polymerization product obtained, the molecular weight controlling agent, the unreacted monomer, and catalyst residue) in an amount of 0.5% by weight based on the monomer, followed by stirring. The reaction mixture was poured into about 6 liters of methanol with vigorous stirring to precipitate the polymer formed. The polymer was recovered by filtration, dissolved in about 500 ml. of 1,2-dichloroethane, and then about 5 liters of methanol was added to the solution to precipitate the polymer again to purify the polymer. The purification procedure was further repeated twice, whereby a faint yellow, flaky polymer was obtained. By drying the polymer for 20 hours at reduced pressure to 50°C, 186.0 g. of the polymer at a polymerization conversion of 97.4% was obtained. The reduced viscosity of the polymer in dimethylformamide at a concentration of 0.1 g./dl. at 30°C was 0.46.

The polymer dissolved in methylene chloride, chloroform, 1,2-dichloroethane, trichloroethylene, toluene, dioxane, and dimethylformamide but did not dissolve in acetone, methanol, and n-hexane.

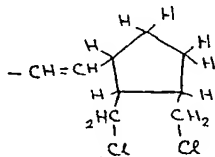
The ring-opening polymerization product thus obtained was fabricated into a film 25 microns thick and the infrared absorption spectra of the film analyzed by means of an infrared absorption spectrometer, IRA—1 type (grating) (made by Nippon Bunko Sha K.K.). The results are shown in Fig. 1 of the accompanying drawings. As is shown in Fig. 1, sharp absorptions are observed at 2940 cm.⁻¹, 1445 cm.⁻¹, 1305 cm.⁻¹, 985 cm.⁻¹, and 735 cm.⁻¹. The absorption at 980 cm.⁻¹ is considered to be based on the trans double bond



Furthermore, the nuclear magnetic resonance spectra of the polymer product were measured by means of a nuclear magnetic resonance spectrometer, R—20 B type, 60 MHz (made by Hitachi Seisaku Sho K.K.), in deuterium chloroform at a concentration of 10% by weight, at 30°C., internal standard material: tetramethylsilane. The results are shown in Fig. 2.

The spectra can be divided into the part of $\delta=6.0-5.0$ (A) and $\delta=4.5-0.5$ (B). The former belongs to the olefin proton and the latter belongs to the proton attached to a saturated carbon. As earlier explained where a ring-opening type polymerization and a vinylene type polymerization is used as the polymerization system, the value of A/B (the area ratio of the domains) is 2/10 in the ring opening type and 0/12 in the vinylene type.

The A/B value measured from the aforesaid spectra of the product was 2.0/10.1, which shows that the polymerization yielding the product was 100% of the ring opening type within the range of experimental error. The product was confirmed to have the following structure:



In addition, large signal observed at $\delta=3.5$ PPM in the domain of B in Fig. 2 belongs to the proton of a $-\text{CH}_2\text{Cl}$ group.

Examples 2—19 and Comparison Examples 1—5:

The same polymerization procedure as in Example 1 was followed except that the amount of chloroacetaldehyde diethyl acetal used in Example 1 as the third component was changed as shown in Table 1 per mole of tungsten hexachloride, or the third components as shown in the same table were used in place of chloroacetaldehyde diethyl acetal. In addition, no third component was used in Comparison Example 1. After the polymerization was completed, the polymers were recovered as in Example 1. The results of the polymerization are shown in Table 1.

TABLE 1

| Example | Third Component | Amount* | Polymer Yield | Conversion |
|-------------------------|-----------------------------------|---------|------------------|------------|
| | | | (g.) | (%) |
| 2 | Chloroacetaldehyde diethyl acetal | 0.5 | 168.3 | 88.1 |
| 3 | —,— | 1.5 | 179.0 | 93.7 |
| 4 | —,— | 4.0 | 180.0 | 94.0 |
| 5 | Acetaldehyde diethyl acetal | 3.0 | 181.8 | 95.2 |
| 6 | Propylene oxide | 2.0 | 172.9 | 90.5 |
| 7 | Ethyl orthoacetate | 2.0 | 175.9 | 92.1 |
| 8 | Ethyl acetate | 2.0 | 164.6 | 86.2 |
| 9 | Tetramethyl orthocarbonate | 1.0 | 167.1 | 87.5 |
| 10 | Acetic anhydride | 1.0 | 162.9 | 85.3 |
| 11 | Di-n-butyl ether | 2.0 | 165.0 | 86.4 |
| 12 | 2-Methylpyridine | 1.0 | 156.6 | 82.0 |
| 13 | N-Nitrosodimethylamine | 1.0 | 160.6 | 84.1 |
| 14 | Nitroethane | 1.0 | 170.8 | 89.1 |
| 15 | Trimethyl phosphate | 1.0 | 165.0 | 86.4 |
| 16 | Triethyl phosphate | 1.0 | 168.3 | 88.1 |
| 17 | Triphenyl phosphate | 1.0 | 156.4 | 81.9 |
| 18 | N,N-Dimethyloctyl amide | 2.0 | 163.0 | 85.4 |
| 19 | Di-n-butylamine | 1.0 | 164.6 | 86.2 |
| Comparison Example 1 | none | — | 47.8 | 25.0 |
| Comparison Example 2 | Benzoyl peroxide | 3.0 | 90.3 | 47.3 |
| Comparison Example 3 | Ethanol | 6.0 | 97.6 | 51.1 |
| Comparison Example 4 | Acetone | 2.0 | 102.9 | 53.9 |
| Comparison Example 5 | Calcium stearate | 1.0 | 73.7 | 38.6 |

(*): The amount of third component added in moles per mole of tungsten hexachloride.

Examples 20—23

The same polymerization procedure as in Example 1 was followed except that the transition metal compounds shown in Table 2 were used in an amount of 0.05 mole percent per mole of the monomer in place of tungsten hexachloride as a component of the catalyst in Example 1. After the polymerization was completed, the polymer formed was recovered as in Example 1. Slightly yellowish polymers at conversion shown in Table 2 were obtained.

TABLE 2

| Example | Transition metal compound | Conversion of polymer (%) |
|---------|-----------------------------------------------------------------|---------------------------------|
| 20 | Molybdenum pentachloride ⁽¹⁾ | 70.5 |
| 21 | W (OC ₆ H ₅) ₆ ⁽²⁾ | 68.8 |
| 22 | MoO ₂ (AcAc) ₂ ⁽³⁾ | 64.1 |
| 23 | Al ₄ W ₃ Cl ₈ ⁽⁴⁾ | 67.6 |

⁽¹⁾: In dimethylformamide at a concentration of 0.1 g/dl. at 30°C.

⁽²⁾: Tungsten hexaphenolate.

⁽³⁾: Molybdenum dioxydiacetyl acetonate.

⁽⁴⁾: Obtained by reducing tungsten hexachloride with aluminum powder.

Examples 24—31.

The same polymerization procedure as in Example 1 was followed except that the organometallic compounds shown in Table 3 were used in an amount of 6 moles per mole of tungsten hexachloride and in an amount of 0.3 moles per mole of the monomer in place of diethylaluminium chloride used in Example 1. After the polymerization was completed, the polymer was treated as in Example 1 to provide a faintly yellow polymer in each case. The results are shown in Table 3.

TABLE 3

| Example | Organometallic compound | Conversion (%) |
|---------|---------------------------------------------------------------------------------------------------------------|----------------|
| 24 | Triethylaluminium | 92.0 |
| 25 | AlEt ₃ -H ₂ O (1:0.5) ⁽¹⁾ | 94.1 |
| 26 | Diethylaluminium hydride | 81.7 |
| 27 | AlEt ₃ -n-C ₄ H ₉ OH ⁽²⁾ | 92.8 |
| 28 | Ethylaluminium dichloride | 86.2 |
| 29 | Ethylaluminium sesquichloride | 89.5 |
| 30 | (CH ₃) ₃ SiOAl(C ₂ H ₅) ₂ ⁽³⁾ | 86.4 |
| 31 | (C ₂ H ₅) ₂ NAl(C ₂ H ₅) ₂ ⁽⁴⁾ | 82.4 |

⁽¹⁾: Modified by water in an amount of 0.5 mole per 1 mole of triethylaluminium.

⁽²⁾: Modified by n-butanol in an amount of 1.0 mole per mole of triethylaluminium.

⁽³⁾: Trimethyldiethyl siloxane.

⁽⁴⁾: Diethylaluminium diethylamide.

Examples 32—38

5 The same polymerization procedure as in Example 1 was followed except that the monomers shown in Table 4 were used in an amount of 1 mole in place of 5,6-dichloromethyl-bicyclo[2,2,1]-heptene-2 used in Example 1. After the polymerization was completed, the polymers obtained were recovered as in Example 1. Thus, light yellow polymers were obtained. The results are shown in Table 4.

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TABLE 4

| Example | Monomer | Conversion (%) |
|---------|--------------------------------------------------------------|-------------------|
| 32 | 5-Chloro-bicyclo [2,2,1]-heptene-2 | 90.8 |
| 33 | 5-Chloromethyl-bicyclo [2,2,1]-heptene-2 | 97.2 |
| 34 | 5,6-Dichloro-bicyclo [2,2,1]-heptene-2 | 94.4 |
| 35 | 5-(α,β -Dichloroethyl)-bicyclo-[2,2,1]-heptene-2 | 91.3 |
| 36 | 5-Chloro-5-methyl-6-chloromethyl-bicyclo [2,2,1]-heptene-2 | 94.7 |
| 37 | 5,5-Dichloromethyl-bicyclo [2,2,1]-heptene-2 | 94.6 |
| 38 | 6-Chloro-5-chloromethyl-5-methyl-bicyclo [2,2,1]-heptene-2 | 93.0 |

Examples 39—58

10 The same polymerization procedure as in Example 1 was followed except that a mixture of 5,6-dichloromethyl-bicyclo[2,2,1]-heptene-2 (hereinafter called "monomer A" and the unsaturated cyclic compounds (monomer B) shown in Table 5 were used in place of monomer A used in Example 1. After the polymerization was completed, the polymers obtained were recovered as in Example 1. The results are shown in Table 5, where the amount of monomer B is given mole % based on the moles of monomer A.

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TABLE 5

| Example | Monomer B | Mole (%) | Conversion (%) |
|---------|--------------------------------------------------------------------|-------------|-------------------|
| 39 | 5-Cyano-bicyclo [2,2,1]-heptene-2 | 30 | 86.4 |
| 40 | 5-Methyl-5-methoxycarbonyl-bicyclo [2,2,1]-heptene-2 | 20 | 88.2 |
| 41 | N-n-Butyl-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalimide | 30 | 80.2 |
| 42 | 5-(2-Pyridyl)-bicyclo [2,2,1]-heptene-2 | 10 | 53.9 |
| 43 | 5-Methoxy-bicyclo [2,2,1]-heptene-2 | 20 | 90.2 |
| 44 | 5-(N,N-Dimethylaminocarbonyl)-bicyclo [2,2,1]-heptene-2 | 10 | 70.3 |
| 45 | 5-Chloromethyl-bicyclo [2,2,1]-heptene-2 | 40 | 96.2 |
| 46 | Cyclopentene | 10 | 85.2 |
| 47 | Bicyclo [2,2,1]-heptene-2 | 10 | 94.6 |
| 48 | 1,4-Dihydro-1,4-methanonaphthalene | 1 | 95.1 |
| 49 | 1,5-Cyclooctadiene | 3 | 88.3 |
| 50 | 5-Phenyl-bicyclo [2,2,1]-heptene-2 | 1 | 94.4 |
| 51 | 2-Phenyl-1,4,5,6-dimethano-1,2,3,4-4a,5,6,6a-octahydronaphthalene | 1 | 93.2 |
| 52 | 3,6-Methylene-1,2,3,6-tetrahydro-cis-phthalic anhydride | 10 | 90.3 |
| 53 | 2,3-Dimethoxycarbonyl-bicyclo-[2,2,1]-hepta-2,5-diene | 20 | 84.8 |
| 54 | 5-Cyano-bicyclo-[2,2,1]-heptene-2 | 10 | 94.2 |
| 55 | —, — | 45 | 80.6 |
| 56 | 5,5-Dichloro-bicyclo [2,2,1]-heptene-2 | 30 | 95.4 |
| 57 | 5-Phenyl-bicyclo [2,2,1]-heptene-2 | 40 | 97.3 |
| 58 | 2-Phenyl-1,4,5,6-dimethano-1,2,3,4,-4a,5,6,6a-octahydronaphthalene | 40 | 95.6 |

Examples 59—63

The same polymerization procedure as in Example 1 was followed except that the molecular weight controlling agents shown in Table 6 were used in an amount of 1.0 mole % based on the monomer in place of n-hexene-1 used as the molecular weight controlling agent in Example 1. After the polymerization was completed, the polymers obtained were treated as in Example 1. Thus, light yellow polymers were obtained. The results are shown in Table 6. In addition, in Table 6, the reduced viscosity was the value measured in dimethylformamide at a concentration of 0.1 g./dl and at 30°C.

TABLE 6

| Example | Molecular weight controlling agent | Conversion (%) | Reduced viscosity |
|---------|---------------------------------------|-------------------|----------------------|
| 59 | Butene-1 | 90.5 | 0.52 |
| 60 | n-Heptene-1 | 94.4 | 0.51 |
| 61 | Octene-1 | 93.0 | 0.52 |
| 62 | 1,4-Hexadiene | 91.2 | 0.49 |
| 63 | none | 92.5 | 2.49 |

Example 64

A mixture of 100 parts by weight of each of the ring-opening polymerization products and ring-opening copolymerization products obtained in Examples 1, 39, 40, 45, 54, 55, 35, 36, 37, 38, and 32; 0.5 parts by weight of a phenolic stabilizer, Yoshinox 2246 (trade name, made by Yoshitomi Seiyaku K.K.) and 2.0 parts by weight of a tin type stabilizer, Stann BM (trade name, made by Sankyo Yuki Gosei K.K.) was kneaded for 5 minutes by means of a Henschel mixer. Each mixture was blended by a roll for 10 minutes at the optimum temperature between 120—200°C for each polymer.

The mixture obtained was hot pressed for 10 minutes at 180—220°C at a pressure of 100 kg/cm² by means of a press and then cold pressed for 10 minutes at a pressure of 100 kg./cm² by means of a water cooled press. For the sake of comparison, the same pressing operation was applied to a commercially available vinyl chloride resin, Kureha S901 (trade name, made by Kureha Kagaku Kogyo K.K., polymerization degree about 1,000) and also to an ACS, ACS 920 resin (trade name, made by Showa Denko K.K.).

About each pressed plate, a notched Izod impact strength, yield strength (tensile strength), elongation percentage at rupture, Vicat softening point, and flame retarding property (by UL method) were measured. The results are shown in Table 7.

TABLE 7

| Run No. | Ring-Opening Polymer | Notched Izod Impact Strength ¹ (kg.cm/cm) | Yield Strength ² (kg/cm ²) | Elongation Percentage at Rupture ² (%) | Vicat, Softening Point ³ (°C) | Flame Retarding Property ⁴ |
|---------|----------------------|---------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|---------------------------------------------|---------------------------------------|
| A | Example 1 | 27.2 | 415 | 100 | 96.0 | 94V-0 |
| B | „ 39 | 28.0 | 450 | 140 | 115.5 | „ |
| C | „ 40 | 27.3 | 412 | 180 | 95.0 | „ |
| D | „ 41 | 20.3 | 440 | 130 | 116.5 | 94V-2 |
| E | „ 45 | 41.2 | 465 | 150 | 91.0 | 94V-0 |
| F | „ 54 | 31.4 | 446 | 130 | 109.0 | „ |
| G | „ 55 | 23.5 | 462 | 140 | 119.5 | 94V-2 |
| H | „ 35 | 26.0 | 414 | 150 | 97.0 | „ |
| I | „ 36 | 28.9 | 426 | 145 | 104.5 | „ |
| J | „ 37 | 43.3 | 460 | 140 | 113.5 | „ |
| K | „ 38 | 29.4 | 436 | 145 | 108.0 | „ |
| L | „ 32 | 70.6 | 388 | 190 | 67.5 | 94HB |
| M | PVC Resin | 2.5 | 520 | 130 | 89.0 | 94V-0 |
| N | ACS Resin | 5.0 | 448 | 60 | 93.0 | „ |

¹ According to ASTM D-256-56³ According to ASTM D-1525-58T² According to ASTM D-638-58T⁴ According to UL-94

WHAT WE CLAIM IS:—

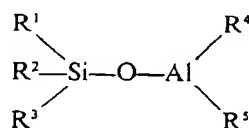
1. A process for the ring-opening polymerization of a chloro-norbornene derivative which comprises subjecting one or more chloro-norbornene derivatives having at least one chlorine atom or a hydrocarbon group substituted with one or more chlorine atoms or a mixture of said chloro-norbornene derivative and at most 50 mole percent of one or more other polymerizable unsaturated cyclic compounds to a ring opening polymerization using a catalyst system prepared from (A) a compound containing a metal-hydrogen and/or metal-carbon bond, said metal being of Group IA, IIA, IIB, IIIB, IVA, or IVB of the Periodic Table (the long form as set out in Encyclopaedia Britannica); (B) a transition metal compound of at least one of tungsten, molybdenum, rhenium, tantalum, and niobium, and (C) at least one of water, an epoxide, an acetal, or orthocarboxylic acid ester, a carboxylic acid anhydride, a carboxylic acid ester, a carbonic acid ester, an ether, an aromatic nitrogen-containing heterocyclic compound, an acid amide, a compound having an N—O bond, an amine, and a phosphorus-containing organic compound, the molar ratio of said (A):(B):(C) being 0.2 to 30.0:1:0.02 to 10.0.
2. A process as claimed in Claim 1, wherein said compound (A) is represented by the formula MR_n , wherein M represents a metal belonging to Group IA, IIA, IIB, IIIB, IVA, or IVB of the Periodic Table; R represents a group having at most 20 carbon atoms selected from an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxide group, a phenoxy group, and a cyclopentadienyl group, a hydrogen atom, or a halogen atom, the groups represented by R_n may be the same or different and said compound (A) contains at least one metal-hydrogen bond or metal-carbon bond; n represents the maximum atomic valence number of said

metal or a positive integer of less than the maximum atomic valence number of said metal.

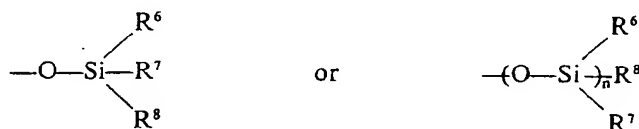
3. A process as claimed in Claim 2, wherein MR_n is selected from compounds represented by the general formulae AlR_3 , AlR_nX_{3-n} and a mixture of compounds represented by said general formula AlR_3 and water, in which the molar ratio of H_2O to AlR_3 is 1.5 where R is selected from an alkyl radical, aryl radical and aralkyl radical, X is a halogen, hydrogen or an alkoxy radical, and n is 1, 1.5 or 2.

4. A process as claimed in Claim 3, wherein the compounds expressed by the general formulae AlR_3 and AlR_nX_{3-n} are selected from trimethyl aluminium, triethyl aluminium, tri-n-propyl aluminium, tri-isobutyl aluminium, trihexyl aluminium, trioctyl aluminium, tribenzyl aluminium, diethyl aluminium monochloride, di-n-propyl aluminium monochloride, diisobutyl aluminium monochloride, di-n-butyl aluminium monochloride, diethyl aluminium monohydride, diisobutyl aluminium monohydride, dibenzyl aluminium monochloride, diethyl aluminium monoethoxide, diisobutyl aluminium monobutoxide, ethyl aluminium sesquichloride, isobutyl aluminium sesquichloride, ethyl aluminium dichloride, isobutyl aluminium dichloride, and ethyl aluminium diethoxide.

5. A process as claimed in Claim 1, wherein said compound (A) is aluminium siloxane represented by the formula

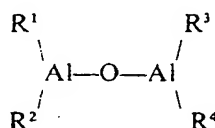


wherein R^1 , R^2 , and R^3 are the same or different and each represents a halogen atom, an alkyl group having at most 10 carbon atoms, or an alkoxy group having at most 10 carbon atoms; R^4 represents an alkyl group having at most 10 carbon atoms; and R^5 represents an alkyl group having at most 10 carbon atoms, an alkoxy group having at most 10 carbon atoms, or a substituent having the formula



(where, R^6 , R^7 , and R^8 , which may be the same or different, each has the same meaning as R^1 , R^2 and R^3 , respectively, and n is a positive integer less than 10.

6. A process as claimed in Claim 1, wherein said compound (A) is a dialumoxane compound represented by the formula



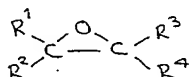
wherein R^1 , R^2 , and R^3 , which may be the same or different, each represents a halogen atom, an alkyl group having at most 10 carbon atoms, or an alkoxy group having at most 10 carbon atoms and R^4 represents an alkyl group having at most 10 carbon atoms.

7. A process as claimed in any preceding Claim, wherein the transition metal compound is tungsten pentachloride, tungsten hexachloride, tungsten pentafluoride, tungsten hexafluoride, tungsten oxytetrachloride, tungsten oxytetrabromide, tungsten oxydichloride, tungsten hexaalkoholate, tungsten hexaphenolate, tetrachlorotungsten diphenolate, tetrachlorotungsten dialcoholate, $Al_4W_3Cl_{18}$, molybdenum pentachloride, molybdenum hexafluoride, molybdenum pentafluoride, molybdenum hexafluoride, molybdenum pentabromochloride, molybdenum pentabromide, molybdenum oxytrichloride, molybdenum oxytetrachloride, molybdenum dioxydiacetyl acetate, dichloromolybdenum dialcoholate, dichloromolybdenum triphenolate, hexacarbonyl tungsten, a complex of tungsten pentachloride and triphenyl phosphine, a complex of tungsten

hexachloride and pyridine, or a complex of tungsten pentacarbonyl and triphenyl phosphine, or the transition metal compound is rhenium pentachloride, rhenium oxytrichloride, rhenium carbonyl ($\text{Re}(\text{CO})_{10}$), rhenium heptachloride, tantalum pentachloride, tantalum tetrachloride, tantalum trichloride, tantalum oxytrichloride, niobium pentachloride, or niobium pentabromide.

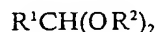
8. A process as claimed in any preceding Claim, wherein the or each of said phosphorous-containing organic compounds has at most 30 carbon atoms.

9. A process as claimed in any preceding Claim, wherein said epoxide is represented by the formula



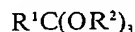
wherein R^1 , R^2 , R^3 and R^4 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where any alkyl or alkenyl moiety has at most 10 carbon atoms, and R^1 and R^3 , and/or R^2 and R^4 , when taken together with the carbon atoms to which they are attached, may form a ring.

10. A process as claimed in any preceding Claim, wherein said acetal is represented by the formula



wherein R^1 and R^2 each represents an alkyl group which may be substituted with one or more halogen atoms.

11. A process as claimed in any preceding Claim, wherein said orthocarboxylic acid ester is represented by the formula



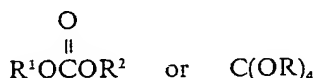
wherein R^1 and R^2 each represents an alkyl group which may be substituted with one or more halogen atoms, where the alkyl group has at most 10 carbon atoms.

12. A process as claimed in any preceding Claim, wherein said carboxylic acid ester is represented by the formula



wherein R^1 and R^2 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where an alkyl or alkenyl moiety has at most 10 carbon atoms, and n is an integer of 1 to 3.

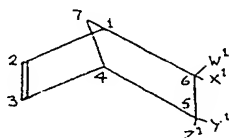
13. A process as claimed in any preceding Claim, wherein said carbonic acid ester is represented by the formula



wherein R , R^1 and R^2 each represents an alkyl group, a cycloalkyl group, a phenyl group, a phenylalkyl group, an alkylphenyl group or an alkenyl group, each of which may be substituted with one or more halogen atoms, where any alkyl or alkenyl moiety has at most 10 carbon atoms.

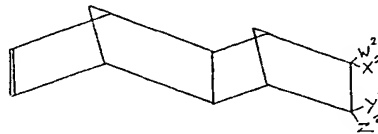
14. A process as claimed in Claim 8, wherein said phosphorous-containing organic compound contains at least one alkyl group, cycloalkyl group, alkenyl group, phenylalkyl group or alkylphenyl group as an organic moiety thereof.

15. A process as claimed in any preceding Claim, wherein said chloronorborene derivative is a compound represented by the following general formula (I) or (II)



(I)

or



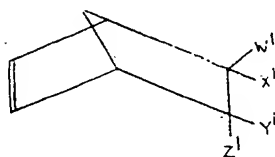
(II)

wherein W^1 , X^1 , Y^1 , Z^1 , W^2 , X^2 , Y^2 and Z^2 are the same or different and each represents a hydrogen atom, a chlorine atom, or a hydrocarbon radical having at most 20 carbon atoms selected from an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, and an aralkyl group, where each of said hydrocarbon groups may be substituted with one or more chlorine atoms and at least one of W^1 , X^1 , Y^1 and Z^1 or at least one of W^2 , X^2 , Y^2 and Z^2 is a chlorine atom or a hydrocarbon group substituted with at least one chlorine atom.

16. A process as claimed in Claim 15, wherein said chloro-norbornene represented by the formula (I) or (II) is 5 - chlorobicyclo[2,2,1] - heptene - 2; 5 - chloromethyl - bicyclo[2,2,1] - heptene - 2; 5 - chloro - 5 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - chloro - 6 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - chloromethyl - 6 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - α - chloroethyl - bicyclo[2,2,1] - heptene - 2; 5 - β - chloroethyl - bicyclo[2,2,1] - heptene - 2; 5 - chloromethyl - 5 - methyl - bicyclo[2,2,1] - heptene - 2; 5,5 - dichloro - bicyclo[2,2,1] - heptene - 2; 5,6 - dichloro - bicyclo[2,2,1] - heptene - 2; 5,5 - dichloro - 6 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - chloro - 6 - chloromethyl - bicyclo[2,2,1] - heptene - 2; 5,6 - dichloro - 5 - methyl - bicyclo[2,2,1] - heptene - 2; 5 - (α,β - dichloroethyl) - bicyclo[2,2,1] - heptene - 2; 5 - chloro - 5 - methyl - 6 - chloromethyl - bicyclo[2,2,1] - heptene - 2; 5,6 - dichloromethyl - bicyclo[2,2,1] - heptene - 2; 5,5 - dichloromethyl - bicyclo[2,2,1] - heptene - 2; 5 - chloromethyl - 5 - methyl - 6 - chloro - bicyclo[2,2,1] - heptene - 2; 5,5,6 - trichloro - bicyclo[2,2,1] - heptene, or 5,5,6,6 - tetrachloro - bicyclo[2,2,1] - heptene - 2.

17. A process as claimed in any preceding Claim, wherein said unsaturated cyclic compound is a cyano-norbornene derivative, ester-norbornene derivative, ether-norbornene derivative, acid anhydride norbornene derivative, imide norbornene derivative, amide norbornene derivative, aromatic norbornene derivative, aromatic nitrogen-containing heterocyclic norbornene derivative, aromatic norbornadiene derivative or ester norbornadiene derivative.

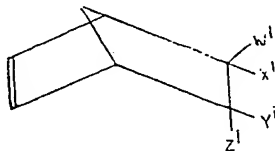
18. A process as claimed in Claim 17, wherein said cyano norbornene derivative is represented by the formula (I).



(I)

wherein W^1 , X^1 , Y^1 and Z^1 are the same or different and each represents a hydrogen atom, a cyano group (nitrilo group), or a hydrocarbon group having at most 20 carbon atoms selected from an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, and an aralkyl group, where each of said hydrocarbon groups may be substituted with a cyano group, at least one of W^1 , X^1 , Y^1 and Z^1 being a cyano group or a hydrocarbon group substituted with a cyano group.

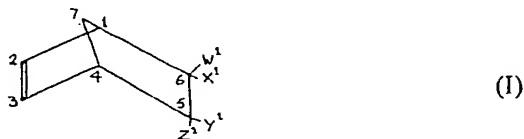
19. A process as claimed in Claim 17, wherein said ester norbornene derivative is represented by the formula (I).



(I)

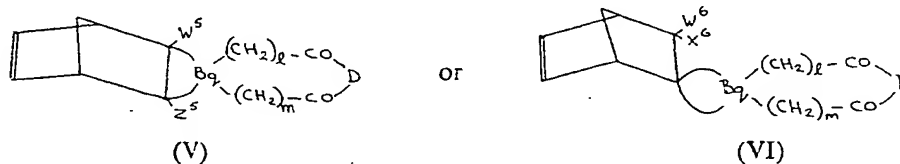
wherein W^1 , X^1 , Y^1 and Z^1 in general formula I each represents a hydrogen atom, an ester group represented by the general formulae $-\text{COOR}^1$ or $-\text{OCOR}^1$, wherein R^1 represents a hydrocarbon group having at most 20 carbon atoms, a hydrocarbon group substituted with an ester group, which is represented by general formula $-\text{R}^2\text{COOR}^1$ or $-\text{R}^2\text{COOR}^1$, where R^1 has the same meaning as above and R^2 represents a divalent hydrocarbon group having at most 20 carbon atoms, or a hydrocarbon group having the same meaning as defined above, at least one of said W^1 , X^1 , Y^1 and Z^1 being the ester group or the hydrocarbon group substituted with an ester group.

20. A process as claimed in Claim 17, wherein the ether norbornene derivative is represented by the formula I.



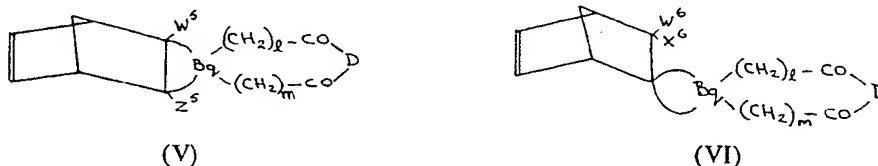
wherein W^1 , X^1 , Y^1 and Z^1 are the same or different and each represents a hydrogen atom, an ether group, or a hydrocarbon group substituted with the ether group, which is represented by the general formula $-R^2OR^1$, where R^1 is as defined above and R^2 represents a divalent hydrocarbon group having at most 20 carbon atoms, or the hydrocarbon group as defined above, at least one of said W^1 , X^1 , Y^1 and Z^1 being an ether group or the hydrocarbon group substituted with an ether group.

21. A process as claimed in Claim 17, wherein said acid anhydride norbornene derivative is represented by the formula V or VI



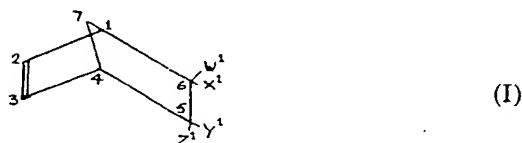
wherein W^5 and Z^5 or W^6 and X^6 are the same or different and each represents a hydrogen atom or a hydrocarbon group having at most 20 carbon atoms; B represents a tetraivalent hydrocarbon group having 4 to 20 carbon atoms; D represents an oxygen atom; l and m each represents independently 1 or 2; and q represents 0 or 1.

22. A process as claimed in Claim 17, wherein said imide norbornene derivative is represented by the formula (V) or (VI).

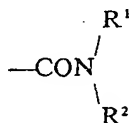


wherein, D represents a group having general formula $>N-R^1$, where R^1 represents a hydrocarbon group having at most 20 carbon atoms or a group having an ester group; B represents a tetraivalent hydrocarbon group having 4 to 20 carbon atoms; l and m each represents independently 1 or 2; and q represents 0 or 1.

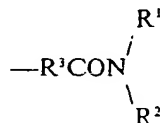
23. A process as claimed in Claim 17, wherein said amide norbornene derivative is represented by the formula (I)



wherein W^1 , X^1 , Y^1 and Z^1 are the same or different and each represents a hydrogen atom, an amide group represented by the general formula

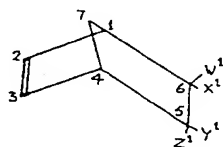


wherein R^1 and R^2 , which may be the same or different, each represents a hydrocarbon group having at most 20 carbon atoms, an amide group-containing hydrocarbon residue represented by the formula



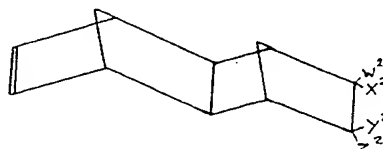
where R^1 and R^2 have the same meaning as above and R^3 represents a divalent hydrocarbon group having at most 20 carbon atoms, or the hydrocarbon group as defined above; at least one of said W^1 , X^1 , Y^1 and Z^1 being the amide group or the amide group-containing hydrocarbon residue.

24. A process as claimed in Claim 17, wherein said aromatic norbornene derivative is represented by the formula (I) or (II)



(I)

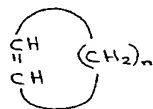
or



(II)

wherein W^1 , X^1 , Y^1 and Z^1 or W^2 , X^2 , Y^2 and Z^2 are the same or different and each represents a hydrogen atom, an alkyl group having at most 20 carbon atoms, a cycloalkyl group having at most 20 carbon atoms, an alkenyl group having at most 20 carbon atoms or an aromatic hydrocarbon group substituted by a hydrocarbon group having at most 30 carbon atoms, said aromatic hydrocarbon group having at most 3 aromatic rings, and at least one of said W^1 , X^1 , Y^1 and Z^1 or W^2 , X^2 , Y^2 and Z^2 being said aromatic hydrocarbon group.

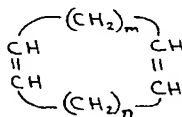
25. A process as claimed in any one of Claims 1 to 16, wherein said unsaturated cyclic compound is represented by the formula (XI)



(XI)

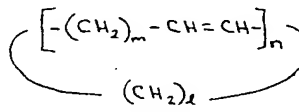
wherein n is an integer of 3 or 5 to 20.

26. A process as claimed in any one of Claims 1 to 16, wherein said unsaturated cyclic compound is a non-conjugated cyclic polyene compound represented by the formula



(XII)

or



(XIII)

wherein l is an integer of 1 to 20 and m and n each is an integer of 2 to 20.

27. A process as claimed in claim 17, wherein said unsaturated cyclic compound is a polycyclic olefinic compound having 2 to 10 rings and 1 to 5 carbon-carbon double bonds.

28. A process as claimed in any preceding claim, wherein said ring-opening polymerisation is carried out at a temperature ranging from -100°C to 200°C .

29. A process as claimed in any preceding claim, wherein said ring-opening polymerisation is carried out in an inert organic solvent.

30. A process as claimed in any preceding claim, wherein said ring-opening polymerisation is carried out in the presence of a molecular weight controlling agent.

31. A process for the ring-opening polymerisation of a chloro-norbornene derivative substantially as hereinbefore described in any one of Examples 1 to 63.

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COMPLETE SPECIFICATION

1 SHEET

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FIG. 1

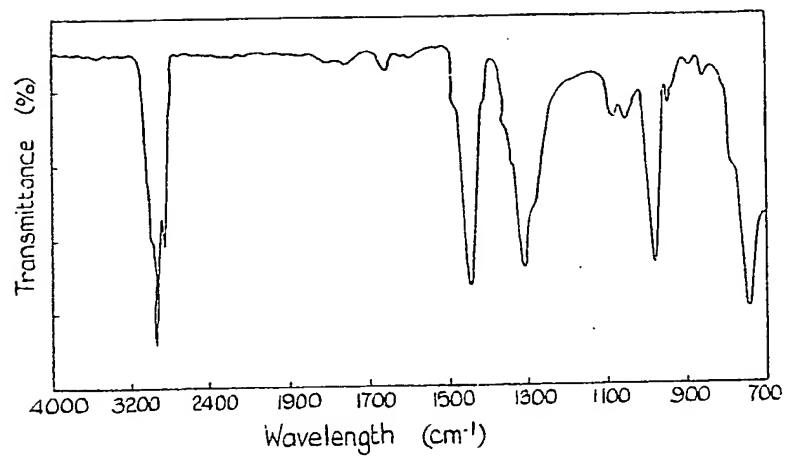


FIG. 2

